Simultaneous Extraction of Sulfur and Mercury from Fossil Fuels Combined with Fluorescence Spectroscopy

BY

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A Dissertation Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMISTRY

April 2013

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN-31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This dissertation, written by **Ibrahim M. Al-Zahrani** under the direction of his dissertation advisor and approved by his dissertation committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY.**

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Dedication

This work is dedicated to my parents, my family, brothers and sisters

ACKNOWLEDGMENTS

I would like to express my acknowledgment to King Fahd University of Petroleum & Minerals for giving me the opportunity to pursue the doctor of philosophy degree in chemistry. It also gives me a great pleasure to thank Dr. T. H. Maung (PhD advisor) who served as my major advisor. My special appreciation is to Dr. C. Basheer (Co-advisor) who has also guided me through the courses of this research and preparation of this report and warmly acknowledged to the remaining members of the committee: Prof. F. Al-Adel, Prof. A. R. Al-Arfaj and Prof. A. Abulkibash for their great support.

I am grateful to the chemistry department chairman Dr. Abdullah J. Al-Hamdan for his support and to Prof. Bassam Ali for his support and advise. My special appreciation and thanks to all faculty members and staff of the chemistry department for their guidance.

Finally, I would like to thank Saudi Aramco Research & Development Center's management and staffs for their support.

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LIST OF ABBREVIATIONS

AXL	:	Arabian Extra Light
ASL	:	Arabian Super Light
AL	:	Arabian Light
AM	:	Arabian Medium
AH	:	Arabian Heavy
SOx	:	Sulfur oxide
EPA	:	Environmental Protection Agency
GC-SCD	:	Gas Chromatography Chemilumenscence Sulfur Detector
XRF	:	X-ray Fluorescence
FT-ICR MS	:	Fourier Transform Ion Cyclotron Resonance Mass
TGA	:	Thermal Gravimetric Analyzer
FTIR	:	Fourier Transform Infrared Radiation
ESEM	:	Environmental Scanning Electron Microscope
NOx	:	Nitrogen Oxide
CO	:	Carbon Mono oxide
RTILs	:	Room Temperature Ionic Liquids
HDS	:	Hydrodesulfurization

HDN	:	Hydrodenitrogenation
HDT	:	Hydrotreating
ILs	:	Ionic Liquids
ODS	:	Oxydeslfurization
DMSO	:	Dimethylsulfoxide
DMF	:	Dimethylformamide
BDS	:	Biodesulfurization
VGO	:	Vacuum Gas Oil
LPME-HFM	:	Liquid Phase Micro-extraction Hallow Fiber Membrane
DLLME	:	Dispersive Liquid Liquid Micro-extraction
PMAFR	:	Porous Membrane Assisted Flow Reactor
2,6 DMBT	:	Dimethylbenzothiophene
2,4 DMBT	:	Dimethylbenzothiophene
2,3 DMBT	:	Dimethylbenzothiophene
2,3,6 DMBT	:	Ttrimethylbenzothiophene
2,3,4 DMBT	:	Trimethylbenzothiophene
DBT	:	Dibenzothiophene

4,MDBT	:	4- Methyl Dibenzothiophene
1MDBT	:	1- Methyl Dibenzothiophene
4,ETDBT	:	4- Ethyl Dibenzothiophene
4,6 DMDBT	:	4,6- Dimethyl Dibenzothiophene
2,4 DMDBT	:	2,4-Dimethyl Dibenzothiophene
3,6 DMDBT	:	3,6- Dimethyl Dibenzothiophene
2,8 DMDBT	:	2,8-Dimethyl Dibenzothiophene
1,4 DMDBT	:	1,4- Dimethyl Dibenzothiophene
1,3 DMDBT	:	1,3- Dimethyl Dibenzothiophene
2 Prop DBT	:	2-Propyl Dibenzothiophene
ASTM	:	American Standard Testing Method
[EMIM][CF_3SO_3]	:	Ethyl Methylimidazolium trifluromethane sulfonate
[BMPY][CH_3SO_4]	:	Butyl methyl pyridiniummethyl sulfate
[EMIM][F_3CSO_2]N	:	Ethyl methyl imidazolium trifluomethylsulfonyl)amide

ABSTRACT

Full Name : Ibrahim Mohammed Saeed Al-Zahrani

Thesis Title : Simultaneous Extraction of Sulfur and Mercury from Fossil Fuels Combined with Fluorescence Spectroscopy

Major Field : Chemistry

Date of Degree : 2013

Fossil hydrocarbons are used as the source of energy in the industrial world. Crude oil fractions such as (gasoline, diesel, and jet fuel) have high amount of impurities such as sulfur containing compounds (0 - 5 %), nitrogen (0 – 0.2%), and metals (e.g. oxygen, nickel, vanadium and iron) ranging from (0 to 0.1% weight). The sulfur and nitrogen containing compounds in gases and liquid fuels poses environmental concerns as well as undesirable in refining processes. Sulfur is the key for the emission of sulfur oxides (SO_x) resulting from combustion of fuels used in transportation. Apart of the sulfur and nitrogen compounds, dissolved mercury (as element) or organomercury compounds have also concern to environmental pollutions. The environmental protection agency (EPA) forced all industry to treat and reduce the emission of all impurities in hydrocarbons particularly sulfur, nitrogen and mercury containing compounds. EPA have set limit for sulfur compounds emission to less than 10 part per million. As a results of EPA regulations, most of refiners started to adapt new technologies which have ability to treat and reduce the complicated sulfur compounds in petroleum product. The current method used at most of industrial refinery is called hydrodesulfurization. It has limited capability for sulfur compounds removal (e.g. dibenzothiophene (DBT), and its derivatives) and this process is expensive and required high quantities of hydrogen. For the first time, we

investigate an alternative approach using porous membrane assisted flow reactor for the simultaneous removal of sulfur and mercury compounds in fossil fuels. The proposed method is suitable to heavy, medium and light crude oil as well as its fractions. In our investigation, nineteen sulfur compounds namely, 2,6-dimethylbenzothiophene (2,6-DMBT), 2,4-dimethyl benzothiophene (2,4-DMBT), 2,3- dimethylbenzothiophene (2,3-DMBT), 2,3,6-trimethylbenzothiophene (2,3,6-TMBT), dibenzothiophene (DBT), 4-methyldibenzothiophen, 2- methyldibenzothiophene + 3-methyldibenzothiophene (3-MDBT), 1-methyldibenzothiophene (1-MDBT), 4- ethyldibenzothiophene (4-EDBT), 4,6-dimethyl-dibenzothiophene, 2,4-dimethyldibenzothiophene (2,4-DMDBT), 3,6-dimethyldibenzothiophene (3,6-DMDBT), 2,8-dimethyldibenzothiophene (2,8-DMDBT), 1,4-dimethyldibenzothiophene (1,4-DMDBT), 1,3-dimethyldibenzothiophene (1,3-DMDBT), 4-ethyl-6-methyldibenzothiophene(4-E-6-MDBT), 2-propyaldibenzothiophene (2-PDBT) and 2,4,8-trimethyldibenzothiophene (2,4,8-TMDBT) were used as model compounds. These compounds are naturally present in the diesel and crude oil samples. All nineteen compounds were monitored before and after porous membrane assisted flow reactor. Gas chromatography sulfur chemilumenascence detector (GC-SCD), X-ray Fluorescence (XRF) and fourier transform ion cyclotron resonance mass spectrometry (FT- ICR MS) were used for quantitation the target analytes. Porous membranes were characterized using thermal gravimetric analyzer (TGA), Fourier transform infrared radiation (FTIR) and scanning electron microscope (SEM).

To achieve our objectives, we design our experiments in four parts. In the first part, liquid-phase micro-extraction technique was developed to optimize the selection of suitable liquid membrane. Various organic solvents and ionic-liquids supported liquid

membranes and acceptor phases were studies in a micro scale. In part two, a flow reactor was designed and applied part one conditions for the removal of sulfur compounds. In part three, simultaneous removal of sulfur and mercury compounds were studied. In part four, to understand the transport mechanism of sulfur and mercury across the membrane, fluorescence and kinetic studies were conducted. The results showed that the porous membrane assisted flow reactor is a promising approach and may be used as alternative method for removal of sulfur, nitrogen and mercury compounds form crude oils as well as its fractions. The results revealed that 58 % (wt/v) of total sulfur including DBT and its derivatives was reduced from Arabian light crude oil, 53 % from Arabian medium crude oil and 44% from diesel, respectively. Nitrogen and mercury compounds removal from crude oils and fractions were also tested. The results revealed that the percentage of total nitrogen removal from light, heavy crude oils and diesel were 49, 44 and 33 %, respectively. Moreover, the mercury was reduced up to 50% from crude oil samples.

ملخص الرسالة

الاسم الكامل: إبراهيم بن محمد بن سعيد الشدوي الزهراني

عنوان الرسالة:إستخدام التقنية المتزامنة لإستخلاص المركبات العضوية الكبريتية والزئبقية من الوقود الحيوي ومشتقاته

التخصص: كيمياء

تاريخ الدرجة العلمية: 2013

الوقود الحيوي ومشتقاته يعتبر مصدر أساسي للطاقة في العالم ويتكون من كربون بنسبة (84-87%) و هيدروجين بنسبة (11-14%) وكبريت بنسبة (0-5%) ونيتروجين بنسبة (0 - 0.2%) ومعادن مثل الحديد والنيكل و الفانيديوم والزئبق وغيرها بنسبة (0- 0.1%). المركبات العضوية الكبريتية والنيتروجينية والزئبقية الموجودة في الوقود الحيوي ومشتقاته تزيد من التلوث البيئي وتعتبر من المركبات الضارة للمواد الحافزة المستخدمة في مصافي البترول وأيضا من أسباب تكون الأمطار الحمضية وزيادة معدل التآكل في المصانع إذا لم يتم معالجتها قبل إستخدامها وتقليل نسبتها إلى أقل من 10جزء من المليون. ولتلك الأسباب أصدرت منظمة البيئة العالمية قوانين لمعالجة المركبات البترولية قبل انبعاثها إلى الغلاف الجوي.

في الوقت الحالي تتم معالجتها بواسطة المواد الحافزة وإستخدام الهيدروجين عند ضغط (30-100 بار) وحرارة 350 درجه مئوية. ولكن هذه الطريقة غير فعالة للتخلص من هذه المركبات المعقدة. إن التحديات المطروحة أمام الباحثين كانت ومازالت لإيجاد طرق أخرى بديلة وغير مكلفة لمعالجة هذه المركبات المعقده. ومن هذه الطرق تم استخدام المواد الصلبة ذات قابلية ألامتصاص واستخدام مذيبات عضوية وأيونية فعالة والفطريات. علما بأن هذه الطرق أثبتت نجاحها في معالجة هذه المركبات العضوية المعقدة واستخلاصها من البترول ومشتقاته ولكن أظهرت بعض المشاكل مثل تغيير جودة المنتج وفقد كميته وصعوبة فصل هذه المواد المستخدمة من المشتقات البترولية. ولهذه الأسباب تم ولأول مره دراسة تطوير تقنية إستخدام الغشاء النسيجي النافذ المساعد لإزالة هذه المركبات المعقدة من البترول ومشتقاته. حيث تم التركيز على (19) مركب عضوي يحتوي على الكبريت مثل: 2,6 – ثنائي ميثايل بنزوثايفين, 2,4 – ثنائي ميثايل بنزوثايفين , 2,3 – ثنائي ميثايل بنزوثايفين , 2,3,6 – ثلاثي ميثايل بنزوثايفين , ثنائي بنزوثايفين ,4 - ميثايل ثنائي بنزوثايفين , 2 - ميثايل ثنائي بنزوثايفين , 1 - ميثايل ثنائي بنزوثايفين , 4 -

أيثايل ثنائي بنزوثايفين , 4,6 - ثنائي ميثايل ثنائي بنزوثايفين , 2,4 - ثنائي ميثايل ثنائي بنزوثايفين , 3,6 - ثنائي ميثايل ثنائي بنزوثايفين , 2,8 - ثنائي ميثايل ثنائي بنزوثايفين , 4,1 - ثنائي ميثايل ثنائي بنزوثايفين , 1,3 - ثنائي ميثايل ثنائي بنزوثايفين , 4 – ايثايل- 6 - ميثايل ثنائي بنزوثايفين , 4-بروبايل ثنائي بنزوثايوفين , 2,4,8-ثلاثي مثايل ثنائي بنزوثايوفين. لكي يتم التوصل إلى الهدف المنشود من هذا المشروع فقد تم تقسيم هذا المشروع إلى أربعة أقسام كما يلي:

1- إختيار الغشاء النسيجي النافذ ذو الفاعلية العاليه لنفاذية هذه المركبات العضوية المعقدة (كبريتية, نيتروجينية وزئبقية).
2- إختيار المذيبات العضوية والأيونية ذات الفاعلية العالية لإستخلاص هذه المركبات المعقدة.
3- تصميم مفاعل يحتوي على غشاء نافذ و مذيب عضوي مناسب موصل بدائرة كهربائية يسمح بدخول المركبات المختاره فقط والتفاعل مع المذيب. علما بأن الجهد المستخدم يساعد على تسارع الأيونات في المفاعل.
4- دراسة كاملة لفهم عملية نفاذية هذه المواد المعقده عبر الغشاء النافذ بإستخدام أجهزه متطورة مثل كروماتوغراف الغازات المحتوية على كاشف مركبات النيتروجين والكبريت وال اكس ري فلورسنس و اف تي ام اس والمايكروسكوب والثيرمل وجهاز تحليل الزئبق.

وقد تم التوصل إلى إستخلاص 58% من المركبات الكبريتية المعقدة من الزيت العربي الخفيف و 53% من الزيت العربي المتوسط و 48% من الزيت الخام الثقيل و 44% من وقود الديزل. و تم إستخلاص المركبات النيتروجينية المعقدة بنسبة 49% من الزيت الخام الخفيف و 44% من الزيت الثقيل و 33% من الديزل وأثبتت نجاح هذه الطريقة لإستخلاص المركبات الزئبقية من الزيت بنسبة 50 % من الزيت.

CHAPTER 1

INTRODUCTION

Eighty-five percentage of energy in the world comes from fossil fuel. Petroleum products such as diesel, kerosene and naphtha contain large amount of sulfur compounds (thiols, sulfides, disulfides and thiophenes) and nitrogen compounds (amines, aniline, indoles and carbazoles). Sulfur compounds generate SO_x and particulate emissions during combustion. Nitrogen compounds also generate NOx during combustion [1]. The sulfur and nitrogen content in petroleum product increases along with the boiling points of the distillate fractions [2]. For instance, naphtha separated from light crude at boiling points ranging from 34 to 149 °C has sulfur content of 0.018 %, kerosene separated at boiling points ranging from 149 to 232 °C has 0.165 % of sulfur, vacuum gas oil separated at boiling point ranging from 343 to 538 °C, contains 2.7% sulfur. Residue oil at boiling points > 538 °C contains 4.1 % sulfur. In addition to sulfur and nitrogen compounds, crude oils and its fractions consists of mercury in ppb to ppm range. Mercury is one of the hazardous environmental pollutants that can affect central nervous system, kidney, and liver damage in human. During the refinery process, mercury in the crude oil can react with metallic surfaces and form amalgams, impairing the proper operation of the equipment, and poisoning the catalyst [3].The sulfur, nitrogen and mercury compounds in petroleum products significantly impact environmental pollutions and undesirable in refining processes [4]. The presence of SOx in the exhaust gas is one of the leading causes of acid rain, causing damage to forests, building materials and poisons catalytic

converters. As a result, the emission of carbon monoxide (CO), nitrogen oxide (NOx) and particulates will increase [5]. A key factor for environmental protection is to control the SOx, NOx and mercury emission in petroleum products to less than 10 ppm [6]. Consequently, the Environmental Protection Agency issued regulations to reduce the sulfur content in petroleum products [7].

There are two major classes of methods for removal of sulfur and nitrogen compounds from petroleum products which includes: (i) conventional and (ii) non-conventional techniques

1.1 Conventional method or hydrodesulfurization (HDS)

In this process, the sulfur compounds are converted to hydrogen sulfide using Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalyst. This process is named hydrodesulfuriztion (HDS) and one of the common approaches in petroleum industries. In HDS very high reaction temperature (350 ºC) and hydrogen pressure (30 to 100 bar) were used. The HDS process is efficient in removing elemental sulfur and few organic sulfur compounds such as (thiols, sulfides and disulfides), but less effective for dibenzothiophene and its derivatives. Same process has also been used for removal of nitrogen compounds. However, carbazol and alkycarbazol are difficult to remove because methyl group in the carbazol and alkycarbazol creates a steric effect that hinders the removal process. Furthermore, application of HDS process for light fractions (contains low sulfur and DBT derivatives) requires special operating conditions which includes highly active catalysts, elevated temperature and pressure [3-8].

1.2 Non-conventional methods

Non-conventional methods have been studied for sulfur and nitrogen containing compounds and metals removal from petroleum products that cannot be removed by currant conventional methods (e.g. DBT and its derivatives).The non-conventional methods able to be operated under moderate conditions without requirements of hydrogen, high temperature, pressure and expensive catalyst. The following techniques have been evaluated as alternative desulfurization methods: (i) solvent or ionic liquids assisted removal (ii) oxidative desulfurization (iii) sorption based sulfur removal (iv) biodesulfirization [9].

1.2.1 Extraction of sulfur compounds by organic solvents

Extraction of organic sulfur and other polar compounds from petroleum product have been investigated at ambient conditions with several organic solvents, as indicated in Table 1 [10]. The organic solvents were selected based on the following properties [11].

1- High selectivity for sulfur compounds and high capacity.

2- Low boiling point of the solvent to be easily regeneration

3- High surface tension of the solvent and insoluble in petroleum product

4- High thermal and chemical stability, and it should be non-toxic

5- Fast separation between solvent and oil fractions

6- The solvent should have low viscosity and low heat of vaporization

Table 1: Organic solvents used for removal of sulfur compounds form petroleum products.

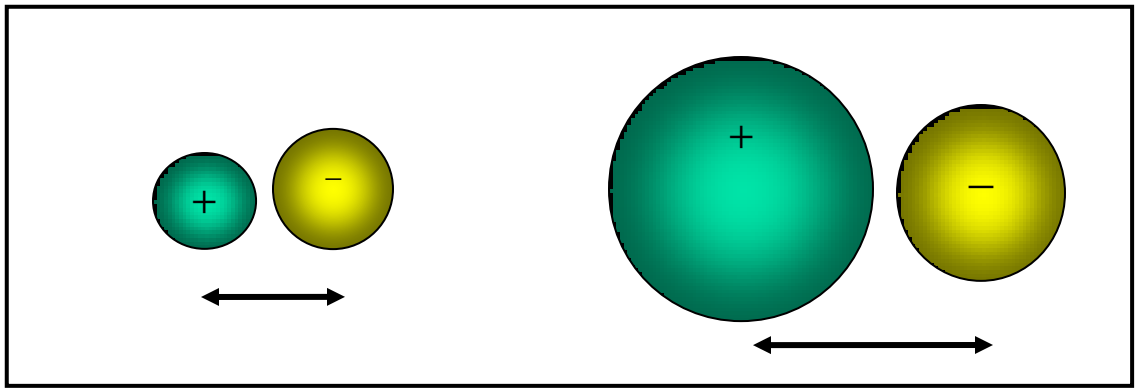
Compound Name	Chemical Formula	Boiling Point (°C)
Acetone	$CH_3C(O)CH_3$	56
Acetonitrile	CH_3CN	82
Butanol	$C_4H_{10}O$	118
Diacetyl	$C_4H_6O_2$	88
Propanol	C_3H_8O	97
Ethanol	CH_3CH_2OH	79
Chloroform	$CHCl_3$	61
Methanol	CH_3OH	65
Furfural	$C_5H_4O_2$	162
Ethylene glycol	$C_2H_6O_2$	197
Propyl acetate	$C_3H_6O_2$	57
Furan	C_4H_4O	31
5-Methylfurfural	$C_6H_6O_2$	187
2-Acetyl 5-methylfuran	$C_7H_8O_2$	100
Furfuryl alcohol	$C_5H_6O_2$	170
Tetrahydrofuran	C_4H_8O	66

Solvent assisted desulfurization doesn't need special equipment. In addition, this process reduces undesirable impurities in petroleum product such as sulfur and nitrogen compounds. Robert reported that this method was able to reduce sulfur content in the range of 60-70% [12]. However, this method changes the fuel's composition because most of aromatic and aliphatic compounds have also been extracted with sulfur compounds. Moreover, more than 5 % of organic solvents will be lost [13].

1.2.2 Extraction by ionic liquids

The room temperature ionic liquids (RTILs) are organic salts with low melting points, mostly at room temperatures. RTILs in general consist of a cation (positive charge) and an anion (negative charge), as shown in Figure 1.

RTILs have many advantages, for example, it does not require high temperature, pressure and the use of hydrogen in sulfur and nitrogen removal process. The results of several works were conducted using RTILs and showed promising for sulfur compounds removal (about 80% reduction) [14]. However, the disadvantages of this process are (i) multi step extraction method (ii) RTILs are extremely expensive than conventional solvents, (ii) Aromatic and some aliphatic compounds were also extracted along with sulfur compounds, resulting reduce octane number.



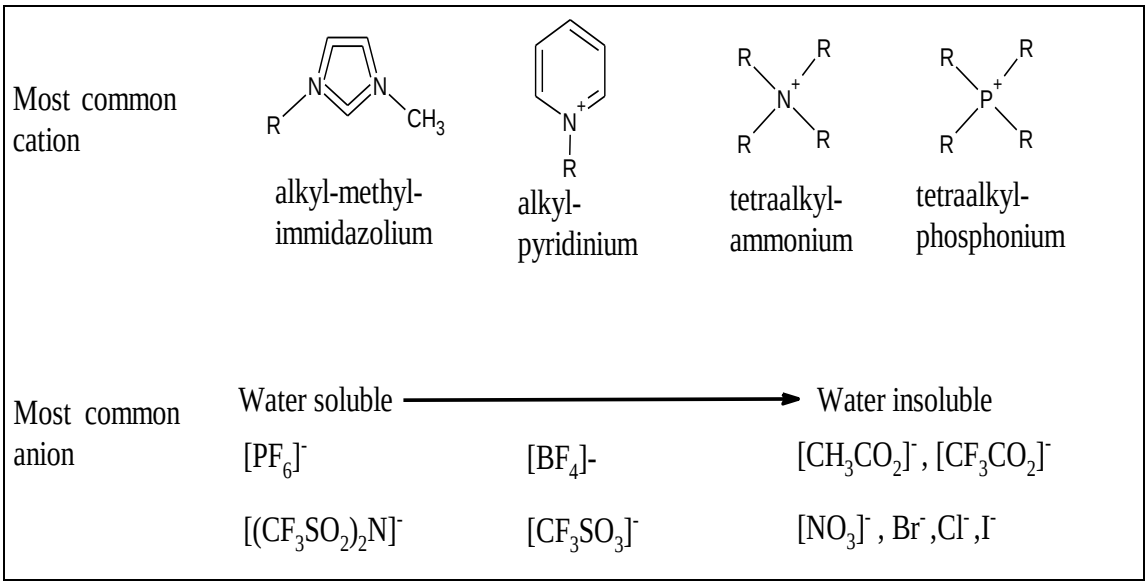


Figure-1: Some common RTILs used for removal of sulfur and nitrogen compounds.

RTILs have been used in various applications such as electrolytes solution in electrochemistry, mixing with an organic solvent or water used for extraction and separation technologies, reagents and catalyst preparation. The following ionic liquids were investigated for desulfurization and denitrogenation at room temperature [14-17].

1- Immidazolium with chloroaluminate anion.
2- Di-alkyl immidazoliumhexaflourophosphate and
3- Di-alkyl immidazoliumtetraflouroburat
4- 1-Ethyl-3-methyl-immidazolium ethyl sulphate [EMIM][EtSO4].
5- 1-Ethyl-3-methyl-immidazolium tetrachloro aluminate [EMIM][AlCl4].
6- 1-Butyl-3-methylimidazolium hexafluorphsphate ($BMIM^+$ $PF6^-$)
7- 1-Butyl-3-methylimidazolium tetrafluorborate ($BMIM^+BF4^-$)

The above RTILs have been selected based on the following properties [15-17]:

1- Non-flammable and non-explosive.
2- High chemical stability and high polarity.
3- Easily regenerated and high efficiency.
4- Not soluble in oil and had very low vapor pressure.

RTILs have different melting points depends on the size of the cation and anion.

Table 2 shows the melting point for several RTILs and physical properties [16-17].

Table 2: Physical properties of RTILs at 25 ºC.

Various Ionic Liquids	Melting point (ºC)	Density (g/ml)	Viscosity (cP)
Ethylammonium nitrate	12.5	1.112	32.1
n-Propylammonium nitrate	4	1.157	66.6
Tri-*n*-butylammonium nitrate	21.5	0.918	637
Di-*n*-propylammoniumthiocyanate	5.5	0.964	85.9
Butylammoniumthiocyanate	20.5	0.949	97.1
Sec-Butylammoniumthiocyanate	22	1.013	196

1.2.3 Oxydesulfurization (ODS)

It has been reported in may papers that oxidation desulfurization (ODS) has been given much interest as alternative technology for deep desulfurization of petroleum product [18]. The ODS process is composed of two stages: first oxidation process followed by liquid extraction using polar organic solvents or ionic liquids [19]. The ODS process converts the thiophene, benzothiphene, dibenzothiopheneand and their derivatives to sulfoxides or sulfones by using several oxidants such as peroxy organic acids, hydroperoxides, nitrogen oxides, peroxy salts, ozone and nitrogen dioxides NO_2 [19]. Figure 2 illustrates the mechanism of ODS process in which dibenzothiophene and thiophene are converted into sulfoxides, sulfones and then extracted by polar solvents such as methanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF) acetone and acetonitrile [20].

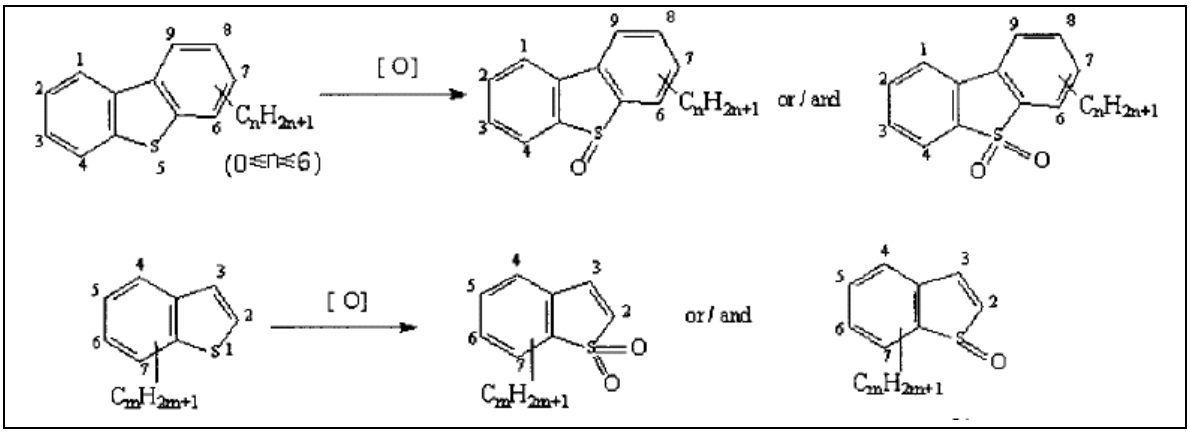


Figure 2. The Oxidation pathway of DBT and BT

The advantages of ODS process are the reaction occurred at low temperature and atmosphere pressure, and no need to use hydrogen. However, the disadvantageous of ODS process are poor selectivity of oxidation and selection of suitable oxidants which produces sulfones or sulfoxide which can be easily removed by polar solvents. Also, this process may reduce the quantity and quality of the petroleum products [21-22].

1.2.4 Adsorption

Desulfurization by adsorption has been reported as alternative method to remove organo-sulfur compounds (e.g. DBT , 4,6 DMDBT and its derivatives) from petroleum products at ambient conditions [23]. Most commonly used sorbents are modified metal oxides, molecular sieves, activated carbon and zeolites [24]. The adsorbents have been selected based on high capacity and selectivity for sulfur compounds, low cost, availability, not having side products, improve the fuel quality by reducing fuel's impurities (e.g. nitrogen, sulfur and metals compounds) and non-toxic [25]. Song reported that Ag^{+},$Cu^{+}$and Zn^{2+} modified zeolites for sulfur removal based on ion-exchange mechanism [8].

The disadvantages of adsorbents methods are (i) adsorption alone cannot reach to deep desulfurization levels for liquid fuel, (ii) most of the adsorbents are not stable and can be easily oxidized, for example Cu (1) to Cu (II) and this is will reduce the selectivity of the sorption process, (iii) fuel additives such as oxygenates and high levels of moistures will quickly deactivates the most of adsorbents.

1.2.5 Biodesulfurization (BDS)

The other alternative method to remove sulfur containing compounds from fossil fuel is by BDS. Sulfur compounds are important for microorganism growth and biological activities [26]. Microorganisms such as *Pseudomanasdelafieldii* and *Rhodococcuserythropolis* are among the many strains of such agents evaluated for deep desulfurization of diesel fuel. There are two pathways for BDS: ring-destructive (degradation) and sulfur-specific desulfurization [27], as show in Figure 3. Microorganisms are capable of growing and desulfurizing organic sulfur compounds at higher temperatures. In addition, several desulfurization bacteria have been isolated from oil containing soils and used for desulfurization [28]. New potential microbial strains called (biocatalysts) has also been studied and shows high potential for sulfur compounds removal [29].

The disadvantageous of BDS methods are (i) low stability of the bacteria in organic medium, (ii) desulfurization rates are extremely slow, (iii) difficulties of strain removal after desulfurization and (iv) low efficiency at higher temperatures [30].

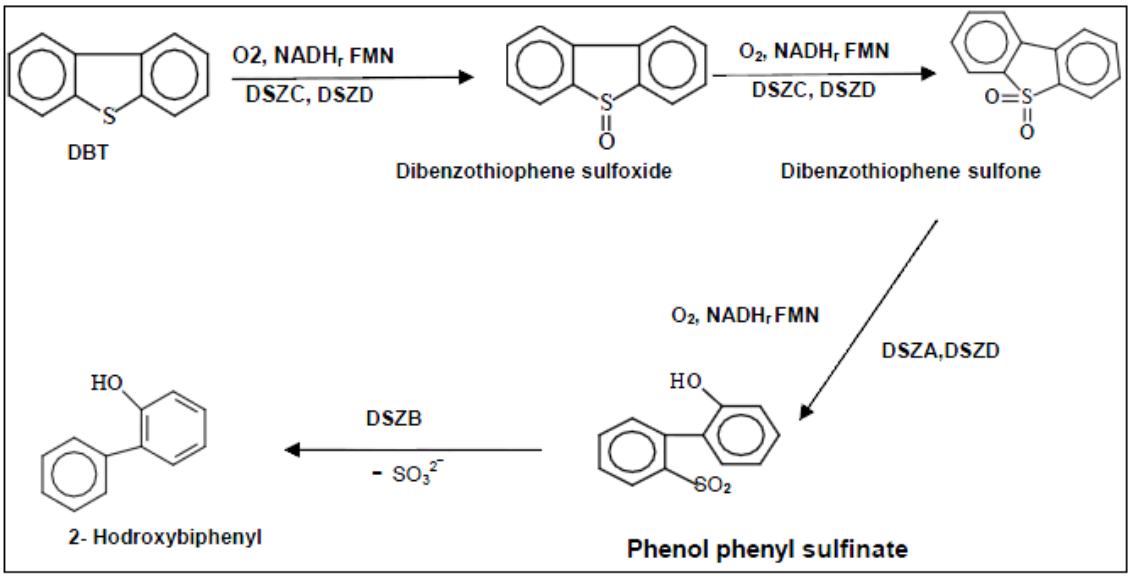


Figure 3. Biodesulfurzaion pathway of DBT

1.3 Mercury removal

Liu reported that combustion of fuel to produce electricity and heat is the largest sources of Hg emission in all countries [31]. Kelly also reported that tracking mercury level is essential for properly operating the plant and control environmental pollutions [32]. Lee highlighted that removal of mercury from petrochemicals is mostly through solid-phase extraction, and carbon-based sorbents are about the most commonly used [33].

1.4 Summary

More attention is now being focused on deep desulfurization and mercury removal of diesel and related products in order to comply with environmental protection and improve the petroleum product quality. To date, HDS using hydrogen gas with Co-Mo/Al2O3 hydrogenation catalysts have been used to remove sulfur and nitrogen containing compounds from natural gas and refined petroleum products. Unfortunately, the cost of this technique is high, the process is usually carried out at high temperatures and pressures and efficiency is reduced in the presence of highly multi-ring sulfur compounds [34]. Consequently, alternative desulfurization techniques such as solvent and ionic liquids assisted methods; oxide sulfurization, adsorbents and bio-desulfurization have a lot of implementation challenges [8]. For the first time, a novel method using porous membrane assisted flow reactor has been proposed to overcome these problems. This method is capable of removing sulfur, nitrogen and Hg compounds simultaneously. This method is a combination of solvents extraction with electrokinetic migration through porous membrane. The porous membrane acting as a barrier between sample and extraction phase and only anlatyes diffuse in to the extraction solvent. In this study

removal of sulfur, nitrogen and mercury compounds of light, medium and heavy crude oil as well as diesel have been investigated. Various experimental conditions with respect to extraction time, selection of solvents, acceptor and donor phase ratios, and quantitative parameters were evaluated to reach to optimize method. Before applying the optimized conditions in flow reactor, experiment were conducted using known amount of sulfur containing compounds (19 organo sulfur compounds). The experiment section was divided into the following categories:

(i) Selection of suitable liquid membrane using organic solvents and its optimization on sulfur extraction.

(ii) Selection of suitable conductive liquid membrane (incorporation of ionic liquid with solvent) and its optimization.

(iii) Design of a flow reactor.

(iv) Application of porous membrane assisted to the petroleum fractions using optimized conditions developed in the previous section (i-ii) in the flow reactor.

(v) Investigation of fluorescence and kinetics study to understand the transport mechanism of simultaneous sulfur and mercury removal.

CHAPTER 2

LITERATURE REVIEW

2.1 Sulfur compounds in crude oil and its products

Crude oils are complex mixture of various compounds. The chemical compositions and physical properties were significantly varied from a crude oil to another depending on the location, origin and types. Crude oils are classified into heavy, medium, light, extra light and super extra light according to their American Petroleum Institute (API) and their gravity. Table 3 shows the characteristics of Arabian crude oils with their API-Gravity and densities. The main elements of crude oils are carbon ranges (84 - 87%), hydrogen (11-14 %), nitrogen (0–0.2%), sulfur (0.05–7.03%) and metals (e.g. oxygen, nickel, vanadium, mercury and iron) ranges from (0 to 0.1% weight) [35]. The ranges of sulfur content in crude oils found in various countries (from 0 to 6.63 %), as shown in Table 4 [36]. However, the mercury content in crude oils in the range of 1-10 ppm depends on the source of the crude oils.

Table 3: Arabian crude oil classification

Crude Oil	API	Density (g/ml)
Arabian Super Light (ASL)	51.3	0.774
Arabian Extra Light (AXL)	39.3	0.828
Arabian Light (AL)	33.2	0.859
Arabian Medium (AM)	30.7	0.872
Arabian heavy (AH)	27.0	0.892

Table 4: Sulfur content in some countries in the world

source	wt. % Sulfur	source	wt. % sulfur
Argentina	0.06 - 0.42	Iran	0.25 – 3.23
Australia	0 – 0.1	Iraq	2.26 – 3.3
Canada	0.12 – 4.29	Italy	1.9 – 6.36
Cuba	7.03	Kuwait	0.01 – 3.48
Denmark	0.2 – 0.25	Libya	0.01 – 1.79
Egypt	0.04 – 4.19	Mexico	0.9 – 3.48
Indonesia	0.01 – 0.66	Nigeria	0.04 – 0.26
Norway	0.03 – 0.67	Russia	0.08 – 1.93
Saudi Arabia	0.04 – 2.92	United Kingdom	0.05 – 1.24
USA	0.29 – 1.95	Venezuela	0.44 – 4.99

More than 200 sulfur compounds have been identified in crude oils, including thiols (mercaptans), sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophene (DBTs), and their alkyl-derivatives [37]. General structures of these compounds are shown below.

Thioles

(R-S-H)

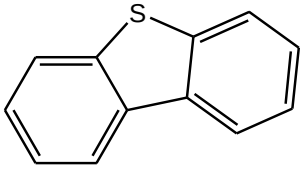
Disulfide

(R-S-S-R)

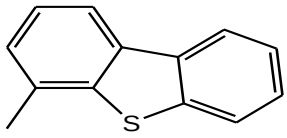
Thiophene

Benzothiophene (BT)

Dibenzothiophene (DBT)



4-Alkyldibenzothiophene



The organic sulfur and nitrogen content in crude oil fractions increase along with the boiling points of the petroleum products, as demonstrated in Table 5 [36].

Table 5. Boiling point of crude oil fractions

Crude Oil Fraction	C-Range	Boiling Point ºC
Light Naphtha	C_6-C_{10}	< 65
Medium Naphtha	C_6-C_{10}	65-105
Heavy Naphtha	C_6-C_{10}	105-175
Kerosene	C_{10}-C_{12}	175-330
Light Gas Oil	C_{12}-C_{20}	260-330
Vacuum Gas Oil	C_{20}-C_{40}	330-550
Residue Oil	>C_{40}	550

2.2 Nitrogen compounds in crude oil and its fractions

Nitrogen compounds are naturally present in crude in crude oils and their fractions. Nitrogen compounds in oil fractions can be classified into two main classes: basic and neutral, [39]. The predominant family in basic nitrogen compounds is the pyridine derivatives, whereas the neutral nitrogen compounds are mainly pyrrole derivatives. It was reported by various authors that nitrogen compounds present in hydrocarbons can also be classified into aliphatic amines, aniline, and two heterocyclic aromatic compound groups with five-membered pyrrolic and six-membered pyridinic ring system [30-39]. Aliphatic amines, anilines and pyridinic compounds form the basic nitrogen compounds, indoles and carbazoles form acid nitrogen components and N-alkyl carbazoles form the neutral nitrogen compounds. Most of nitrogen in heavier petroleum fractions is present as aromatic heterocycles with multiple rings such as quinolines, acridines, indoles and carbazoles and benzocarbazoles. The nitrogen compounds grouping and identification in petroleum fractions and their structures are shown in Table 6. Crude oil fractions generally contain low level of organic nitrogen compounds range from 20 to 1000 ppm, as illustrated in Table 7. As like sulfur compounds, nitrogen content strongly increases with increasing boiling point of the crude oil fractions [40]. As a results, the higher the boiling point of a fuel, the higher nitrogen and sulfur content [41]. For instance, the middle–distillate (diesel fuel) has a higher sulfur and nitrogen content than the lower–boiling–range gasoline fraction. Vacuum gas oil (VGO) has also sulfur and nitrogen content higher than naphtha and kerosene.

Table 6. Typical nitrogen compounds in petroleum products

No.	**Molecules**	**Class Type** **Acid /Base**	**Strength**
1	Indoles	Acids	Very Weak
2	Carbazoles	Acids	Very Weak
3	Amides	Acids	Weak
4	Quinolones	Acids	Weak
5	Caroxylic Acids	Acids	Strong
6	Phenolic Amines	Base	Very Weak
7	N-Alkyl Indoles	Base	Weak
8	Anilines	Base	Strong
9	Quinolines	Base	Strong
10	Pyridines	Base	Strong
11	N-Alkyl Carbazoles	Neutral	Strong

Table 7: Nitrogen content in petroleum fractions

Crude Oil Fraction	C-Range	Boiling Point ^{o}C	Nitrogen ppm
Heavy Naphtha	C_6-C_{10}	80-180	2
Gas Oil	C_{12}-C_{20}	200-400	430
Vacuum Gas Oil	C_{20}-C_{40}	350-560	1200
Residue Oil	> C_{40}	550	> 1200

2.3 Mercury compounds in crude oil and its products

Mercury is another environmental pollutant present at low concentration in crude oils and their fractions. Elisabeth reported that combustion of fuel to produce electricity and heat is the largest sources of Hg emission in all countries [3]. About 62 % of Hg emission from fuel combustion worldwide occurs in Asia. Carbon-based sorbents have been used for removal of mercury through solids phase extractions. However, this system does not work effectively for removal all species of mercury, [42]. Further research is needed to achieve significant removal of mercury from all petroleum products as well as gases.

2.4 Impact of sulfur, nitrogen and mercury containing compounds

2.4.1 Environmental impact

The presence of SO_x and NOx in exhaust gas is one of the leading causes of acid rain. Nitrogen oxides (NOx) and sulfur dioxide (SO_2) reach to the ground through dry deposition and wet-deposition, as shown in Figure 4. These pollutants were easily bound to the atmospheric particles and transport globally. Most wet acid deposition forms when nitrogen oxides (NOx) and sulfur dioxide (SO_2) are converted to nitric acid (HNO_3) and sulfuric acid (H_2SO_4) through oxidation and dissolution. Wet deposition can also form when ammonia gas (NH_3) from natural sources is converted into ammonium (NH_4). The increased acidity in water caused by acid rain can cause the death of fish and other aquatic as well as acid rain harms vegetation and inhibit the growth of trees. Acid rain adds hydrogen ions to the soil which reacts with soil minerals, displacing calcium, magnesium and potassium [43].In addition, air quality will be effected by sulfur emissions in the atmosphere.

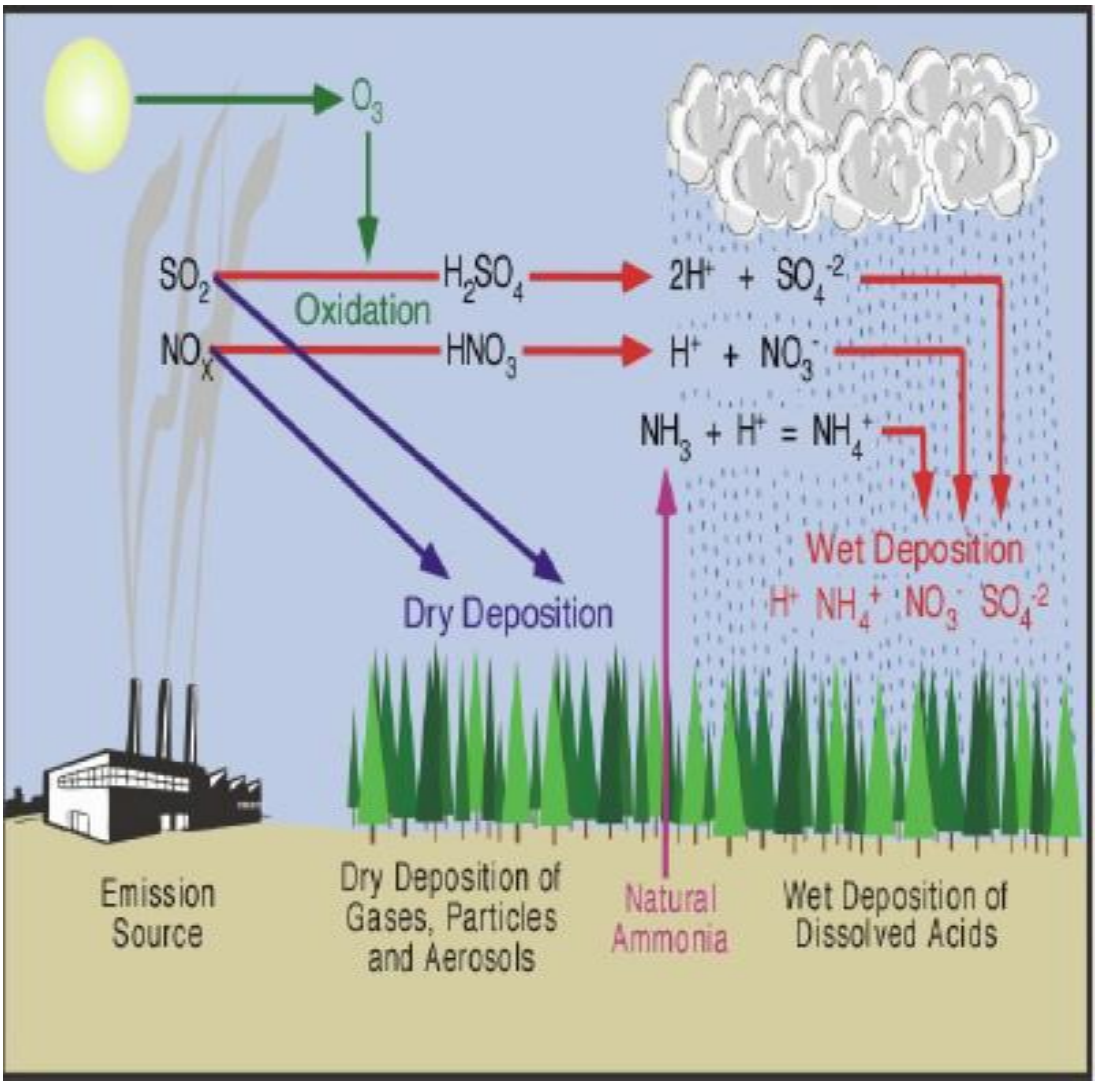


Figure 4: SO_x and NO_x emission sources

2.4.2 Health impact

Sulfur is important for the functioning of proteins and enzymes in plants and animals. Inhalation of excess sulfur and mercury on animals are mostly damage brain and affect the nervous system. Excess amount of hydrogen sulfide, nitrogen oxide and mercury > 10 ppm release into air are extremely affecting the human health. Sulfur dioxide can affect the respiratory system and functions of the lungs and irritate the eyes. When sulfur dioxide irritates the respiratory causing coughing, mucus secretion and aggravates. The presence of sulfur and nitrogen in transportation fuel poisons catalytic converters which are used in cars to clean the exhaust outlets from particulates such as (CO, NO_x) The sulfur, nitrogen and mercury compounds are also undesirable in refining processes because they increase the corrosion rate during the gas refining process, and they contribute to the formation of deposits and black powder [44-46].

2.5. Legislation on sulfur, nitrogen and mercury limit

Due to high impact of both sulfur and nitrogen containing compounds, the Environmental Protection Agency (EPA) issued regulations to control the sulfur content in gas and liquid fuel to less than 10 ppm, as shown in Table 8 [46].

Table 8: Changes of Sulfur specification Europe and US

Country	Europe 2000	Europe 2009	US 2000	US 2009
Sulfur ppm	350	< 10	500	< 10

To overcome this issue, various processes have been developed to remove sulfur and nitrogen compounds from petroleum products. This includes hydrodesulfurization (HDS), oxidative desulfurization (ODS), adsorption, liquid-liquid extraction and biodesulfurization.

2.6 Hydro-desulfurization (HDS) and Hydro- denitrogenation (HDN)

Sulfur and nitrogen containing compounds can be removed in petroleum refinery using conventional HDS process. In many publications reported that the hydrotreating (is a process for catalytically stabilizing petroleum products or for removing elements from products or feed stocks (crude oils) by reacting with hydrogen). This process is the most common for fuel oils desulfurization. In typical HDS processes, oil and hydrogen are introduced to a reactor which is packed with suitable HDS catalyst. The conditions of the reactor: temperature 300 – 400 ºC, and pressure 30-200 atmosphere depends of the feed , but the temperature and pressure in hydrotreating processes must be further elevated to achieve higher HDS treatment [47]. However, this process is not able to remove DBT and its derivatives. Conventional technologies such as hydrocracking (is a catalytic process which heavy crude oil, residue, is converted to more desirable lower boiling products such as kerosene, middle distillates, lubricating oils and fuel oils) and hydrotreating provide solution to refiners for the production of clean transportation fuels [48]. Shiraishi reported that several catalysts were developed, for hydrotreating process, including cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides and vanadium oxide. The most general use catalysts today are the cobalt and molybdenum oxides on alumina catalysts because highly selective, applicable, easy to regenerate and resistant to poisons. The catalysts (Co-Mo, Ni-Mo) and (Co-Ni-Mo) are

common used for HDS. The selection between Co-Mo and Ni-Mo ratio is highly depends on the natural of feed, operating, conditions and specifications [49-50].

Ni-Mo are used when heavy feeds are processed and contain high level sulfur and nitrogen compounds. A Co –Mo catalysts are also selective for sulfur compound removal and Ni-Mo catalysts are highly selective for nitrogen compound removal, although both catalysts will remove both sulfur and nitrogen [51]. It was highlighted that the sulfur level was reduced to the acceptable amount using catalyst which contains oxides groups [52]. DHS, HDN, aromatic hydrogenation and olefin hydrogenation are done in the hydrotreating reactor. DBT reactions follow two routes: direct HDS and hydrogenation. In the direct desulfurization route, the carbon-sulfur bond is broken and then sulfur released as shown in the Figure 6. Whereas, in the hydrogen route (Figure 5), one of the aromatic molecule is hydrogenated then the carbon-sulfur bond becomes weaker and is broken to release the sulfur. It has been reported that ultra sulfur can be achieved using hydrogenation route

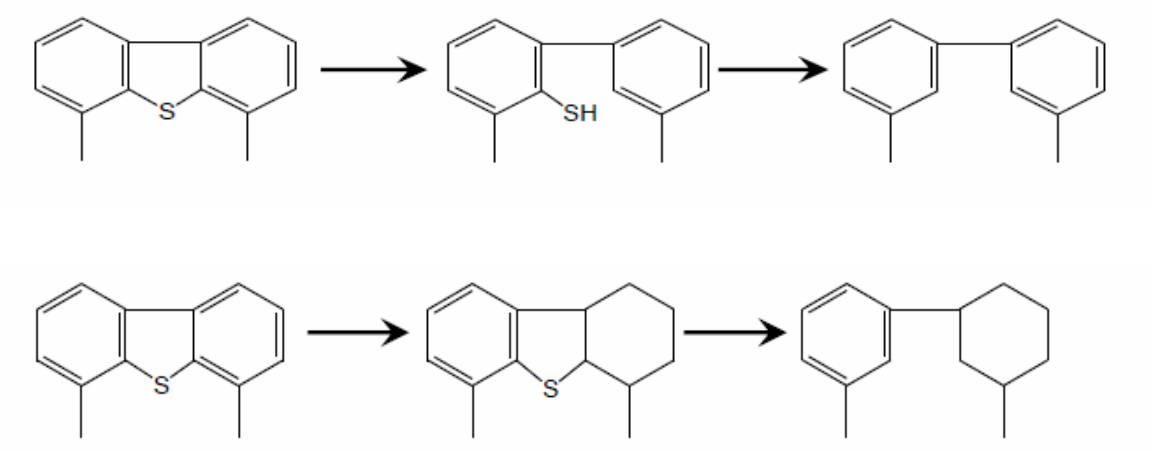


Figure 5: Direct Desulfurization Route and Hydrogenation Route

However, Ni–Mo catalyst have a higher hydrogenation activity than Co-Mo. Song reported that hydrodesulfurization is carried out in a single reactor over supported catalysts containing sulfides of Co-Mo or Ni-Mo or combination in the temperature and hydrogen pressure 320-400 °C and 20-60 bars, respectively[1]. Also, they reported HDS is carried-out in two-stage hydrotreating process and octane number improvement. Torrisi listed various conditions (temperature, hydrogen pressure) of hydrotreating process, as shown in Table 9 [52]. This process is selected based on the feed type.

Table 9: Hydrotreating process for various fractions

Feed	Process Hydrotreating	Temperature ºC	H_2 Pressure Mpa	H_2 Consumption Nm^3/m^3
Naphtha	HDT	320	1-2	2-10
Kerosene	HDT	330	2-3	5-10
Atm. Gas Oil	HDT	340	2.5-4	20-40
Vac. Gas Oil	HDT	360	5-9	50-80
Atm. Residue	HDT	370-410	8-13	100-175
Vac. Gas Oil	HDT	380-410	9-14	150-300
Vac. Residue	HDT	400-440	10-15	150-300

Bjerre reported that HDS using hydrogen gas and hydrogenation catalysts such as Co-Mo/Al_2O_3 to achieve removal of sulfur-containing compounds from natural gas and refined petroleum in a hydrotreater [53]. The cost of this technique is high, and the process is usually carried out at high temperatures and pressures. Total sulfur conversion is affected by different temperature regimen [54]. Augueda reported that HDN reactions occur via a complex reaction, involving hydrogenation of aromatic followed by carbon–nitrogen broken. The reaction mechanism is shown in the Figure 6 [55].

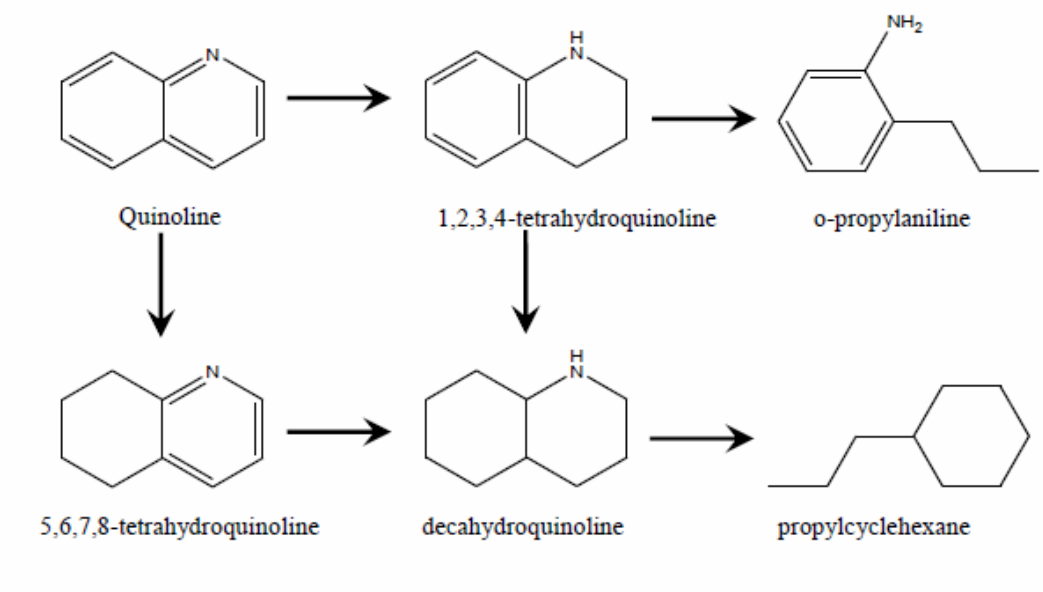


Figure 6: HDN pathway for Qunoline .

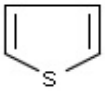
It was reported by many authors that nitrogen and aromatic compounds are also negatively impact the HDS efficiency. The basic nitrogen compounds are the most poisons for the catalysts. Hydrocracking reactions are also called hydrotreating, including hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) [33-56].

Figure 7 shows that the sulfur and nitrogen compounds increase with the boiling point and the sulfur and nitrogen compounds reactivity decrease with increasing boiling point and molecular weight.

The following reactions show how sulfur is converted to hydrogen sulfide and hydrogen in the hydrotreating process.

Sulfides $R\text{-}S\text{-}R + 2\,H_2 \longrightarrow 2RH + H_2S$

Disulfides $R\text{-}S\text{-}S\text{-}R + 3\,H_2 \longrightarrow 2RH + H_2S$

Thiophene  $+ 4\,H_2 \longrightarrow CH_3\,(CH2)_2CH_3 + H_2S$

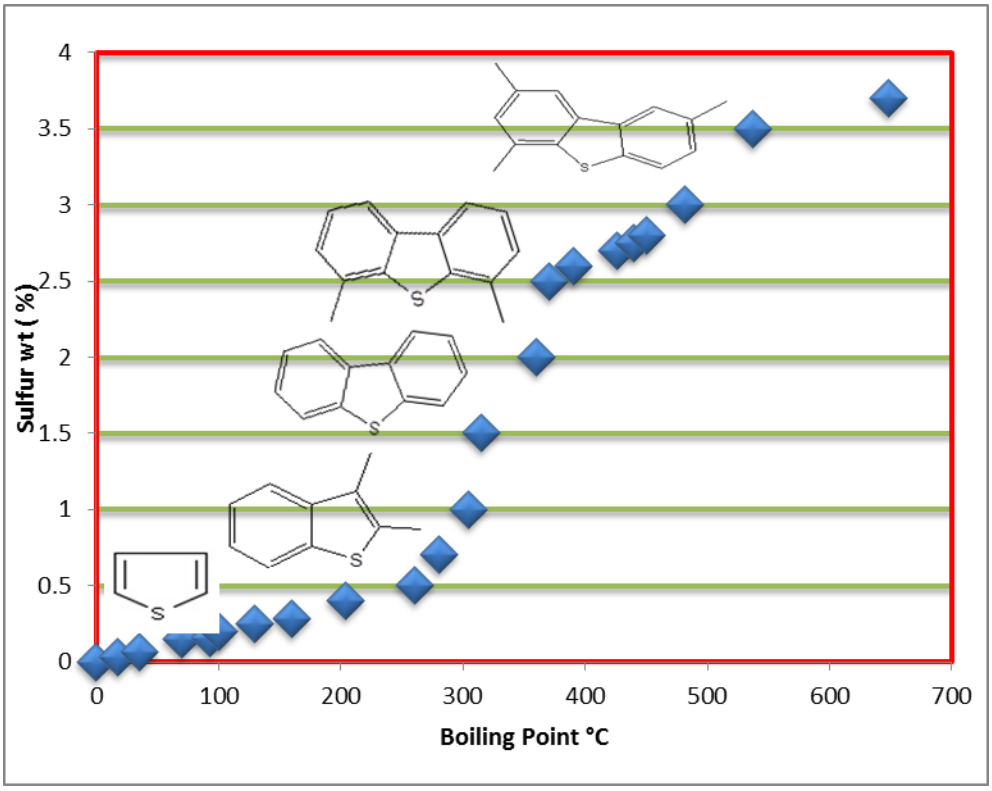


Figure 7: sulfur and nitrogen compounds versus boiling points

Because this process (conventional method) requires high-pressure reactors and vessels, it needs huge investments. To overcome these challenges the non-hydrogen-consuming desulfurization techniques such as liquid-liquid extraction, adsorption, biodesufurization, membrane and oxidation have been investigated. The alkyl dibenzothiophene and alkycarbozole are the most difficult compounds to be removed by HDS because of the steric hindrance of the sulfur and nitrogen atoms. Accordingly, alternative hydrodesulfuruization techniques have been investigated as follows:

2.7 Non-conventional methods

Many researchers reported that advanced alternative technologies were needed to minimize undesirable impurities in fuel oils to improve the petrochemical products quality.

2.7.1 Desulfurization and denitrogenation using liquid-liquid extraction

Various organic solvents such as methanol, acetone and acetonitrile were evaluated for direct sulfur and nitrogen compounds removal from crude oils and fractions. Also, various ionic liquids were evaluated for direct removal of sulfur and nitrogen compounds from petroleum products. Bailes studied the possibility of the sulfur compounds and aromatic hydrocarbons removal from model compound and light oil by extracting with organic solvent such as acetonitrile, dimethyl sulfoxide and tetramethylenesulfone at room temperature conditions. The results revealed that 5 minutes is needed to achieve the extraction equilibrium between light oil and organic solvents and the phase separation was achieved in about 10 seconds. He also highlighted that acetonitrile is more suitable solvent for light distillation products to achieve deep desulfurization [57].

A new method using a photochemical reaction and liquid–liquid extraction has been developed for deep desulfurization. They concluded that DBT was removed from a model compound by using UV light followed by acetonitrile. This method (photochemical reactions UV radiation, followed by acetonitrile extraction) to remove sulfur compounds from straight-run light gas oil. In this procedure, sulfur content was reduced from 0.2% to 0.05% weight from gas-oil [1,52,59].

Jess examined the sulfur compounds and nitrogen compounds removal form model compounds and diesel at ambient temperature and pressure using ionic liquids such as butylmethylimidazolium (BMIM) chloroaluminate and also halogen-free ionic liquids like BMIM-octylsulfate. The results showed that these ionic liquids were capable to remove sulfur and nitrogen content to less than 50 ppm [16].

Zhang investigated the sulfur compound and nitrogen compounds removal using two types of ionic liquids (1-alkyl 3 methylimizolium, tetrafluoroborate, hexafluorophosphate and trimethylamine hydrochloride). The authors concluded that these ionic liquids were highly selective and applicable for sulfur and nitrogen removal from fuels oils. These ionic liquids can easily be regenerated by distillation process [11].

Holbrey used several ionic liquids (1-Butyl-3-methylimidazolium tetrafluroborate ($BMIMBF_4$), 1-Butyl-methylimidazolium hexafluorophospate ($BMIMPF_6$), and 1-Ethyl-3-methylimidazolium hexafluorophospate ($EMIMBF_4$) with the 1-alkyl being ethyl and butyl) for sulfur and nitrogen compounds removal from model compounds and fuel oils. Authors concluded that: These ILs have negligible absorption for alkenes and very low absorption for olefins. $BMIMPF_6$ has the highest absorption capacity for organosulfur and nitrogen compounds, followed by $BMIMBF_4$ [17].

Holbery evaluated the performance of four different ILs: imidazolium, pyridinium, pyrrolidinium, and quinoliniumfor sulfur and nitrogen compounds removal from model compounds and real diesel. They demonstrated that the cation molecule has more effect on the extraction capacity, comparing with the anion molecules [60].

Gao studied several types of ILs for sulfur and nitrogen containing compounds extraction from model oil. The extraction process time such as temperature, IL: oil weight ratio, and different sulfur species extractability have been studied. He also investigated the effect of the anion molecules using three ILs [BMIM][PF6], [BMIM][BF4], and [BMIM][FeCl4]. He reported that IL with the longest alkyl group showed higher performance and the DBT compounds have been extracted by ILs more due to more interaction between the IL and the aromatic sulfur compounds [61].

2.7.2 Oxidative Desuifurization (ODS)

In 1967, This alternative method for sulfur containing compounds removal was patented. Zhang reported that the oxidation of sulfur containing compounds in liquid phase is highly possible due to the strong affinity between oxygen and sulfur without rupture of C-C and C- S bonds [62]. It was reported by various authors that the ODS process occur in two steps: (i) 1st process oxidation using catalyst (metal oxide) e.g. ZnO or NiO in the presence of H_2O_2, in this process sulfur convert to sulfoxides and then convert to sulfones (ii) in the 2nd process the sulfone extracted by using polar solvents, as shown in Figure 8 [7,8,15,24,52]. Holbrey reported that the mechanism of sulfur compounds removal from gas phase using metals oxides (ZnO or NiO) in the present of oxygen can be done initially, the sulfur compounds adsorbed at the surface of the catalyst and then sulfur can be de-adsorbed at higher temperature > 150 °C, as shown in Figure 9 [60].

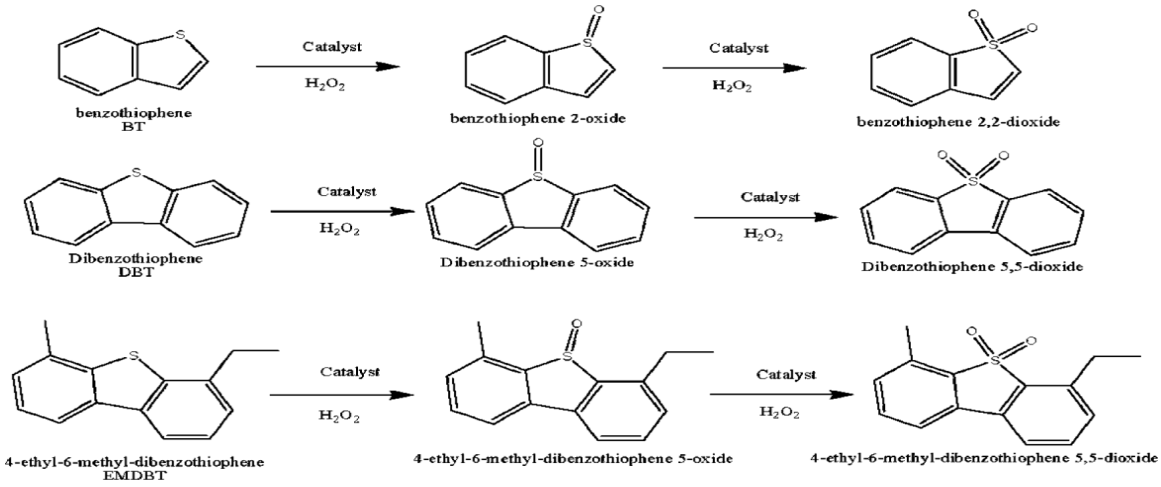


Figure 8: ODS pathway in presence of catalyst of BT, DBT and alkyl-DBT

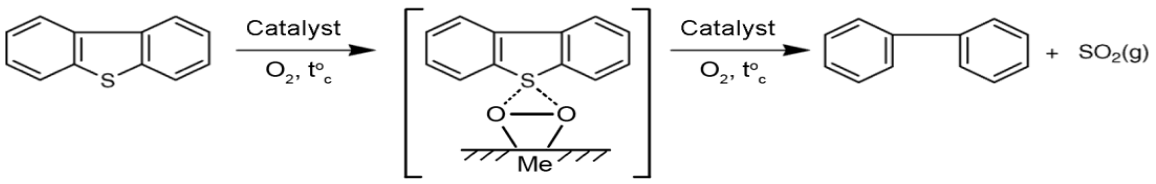


Figure 9: ODS pathway for DBT with support of catalyst and O2

2.7.3 ODS process using oxidation followed by extraction or heat

Many authors reported that the sulfur compounds can be easily converted to sulfoxides and then changed to sulfones using H_2O_2 and then easily separated by extractive with polar organic solvent such as methanol or acetone or absorbent or heat, as shown in Figure 10. This method was conducted at atmospheric pressure and temperature 180- 250 °C. This method is applicable for sulfur containing compounds removal from hydrocarbon fuels to below 150 ppm [7,8,15]. Zannikos studied the ODS using petoxyacetic acid to oxidize the organosulfur compounds in a diesel fuel. Then, polar organic solvents (methanol and dimethyl formamide) were use as solvent to extract sulfur compounds. However, these solvents removed much of the other hydrocarbons from the sample with sulfur compounds which will affect the quality of fuels [18]. Tam investigated the possibility of HDS from gas oil and other petroleum fractions using nitrogen oxide or nitric acid. The sulfur compounds were easily oxidesed and then removed by polar organic solvents [64]. The ODS method was examined for HDS at ambient pressure and low temperature (0-30 °C), using H_2O_2 or nitrogen oxides as oxidants and then polar solvent was used to remove sulfur compounds [65]. Yen reported that organic sulfur compounds can be removed from fossil fuel by combination of oxidative desulfurization with the ultrasound process. This study concluded that to < 10 ppm of Sulfur compounds removal could be achieved using this process[66].

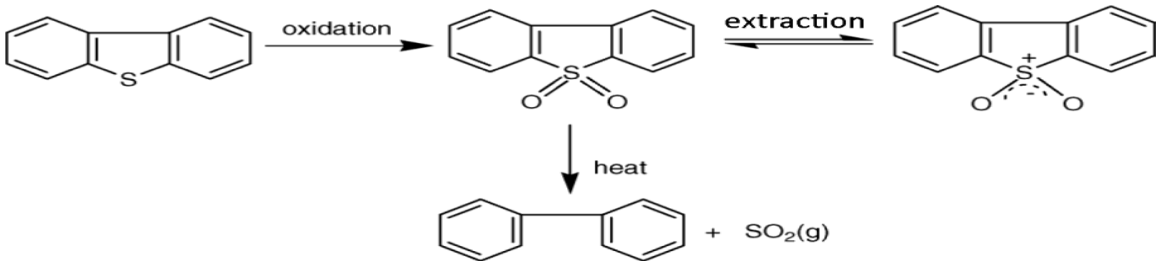


Figure 10: ODS process (oxidation followed by extraction) of DBT

2.7.4 Desulfurization using Adsorbent

An alternative HDS method has been developed by Phillips in 1998. In this procedure, hydrotreating process can be avoided resulting reducing hydrogen consumption. This method can save a refinery significant operation costs. Phillips process is carried out in the presences of hydrogen and modified zinc oxide. Chmisorpotion with zinc as zinc sulfide have been used to convert organ-sulfur to hydrogen sulfide. This process was carried out uisng proxy acetic acid in which 4,6-dimethyldibenzothiophene was converted to sulfoxide and sulfones. They concluded that this process was able to reduce the sulfur content and nitrogen compounds to < 10 ppm [67]. Larrubia evaluated the removal of sulfur and nitrogen compounds (benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene, indol and carbazole) form fractions using alumina and zirconia as adsorbents [68]. Robert investigated the sulfur compounds removal (thiophene, benzothiophene and dibenzothiophene) using $Ru(NH_3)_5(OH_2)^{2+}$. However, they concluded that DBT cannot be removed by this process [12]. Akzo Nobel developed a new HDS catalyst, known as Nebula, which is based on Ni-Mo and contains (15-20 %) of active material than current HDS process. Nobel reported that sulfur compounds can be reduced to 10 ppm in diesel fuel, but the new catalyst requires higher hydrogen consumption rates. Velue investigated sulfur containing compounds removal using ion exchanged zeolite, from model and jet fuels at 80 ºC. They also examined Ni(II)-Y,Zn(II)-Y for sulfur and nitrogen compounds removal. This method was able to reduce sulfur compounds from fuel oils [1]. Figure 11 shows the mechanism of sulfur compounds removal using adsorbent.

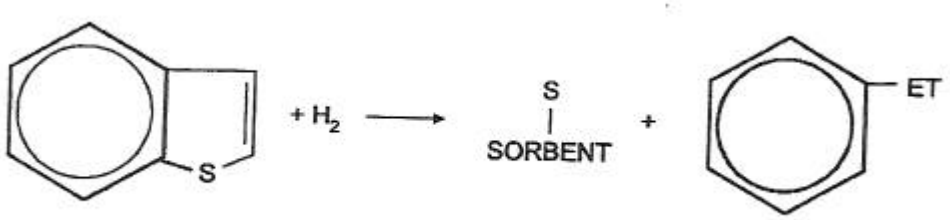


Figure 11: Desulfurization pathway of BT using adsorbent

2.7.5 Desulfurization by biodesulfurization (BDS)

BDS method is used as alternative technology for sulfur compounds removal from fossil fuel by using biological. Microorganisms are required sulfur in order to grow and sulfur occurs in the structure of some enzyme. Recently, Some reviews have published that microorganisms can consume the sulfur in thiophenic compounds such as (DBT, 4,6-DMDBT) and reduce the sulfur content in fuel oils [70]. There are two main pathways have been reported for (BDS):

1- Destructive BDS

In this pathway dioxygenation is carry out at the aromatic ring of DBT, followed by cleavage of the ring. This process leads to 3-hydroxy-2-formylbenzothiophene as product. In this process carbon content is lower than DBT, but no desulfurization has been has been occurred in this process.

2- Specific oxidative BDS

This process was proposed by Kilbaneet. In this pathway, the sulfur in DBT is converted to sulfoxide, sulfone, sulfinate and hydroxybiphenyl, as shown in Figure 12.

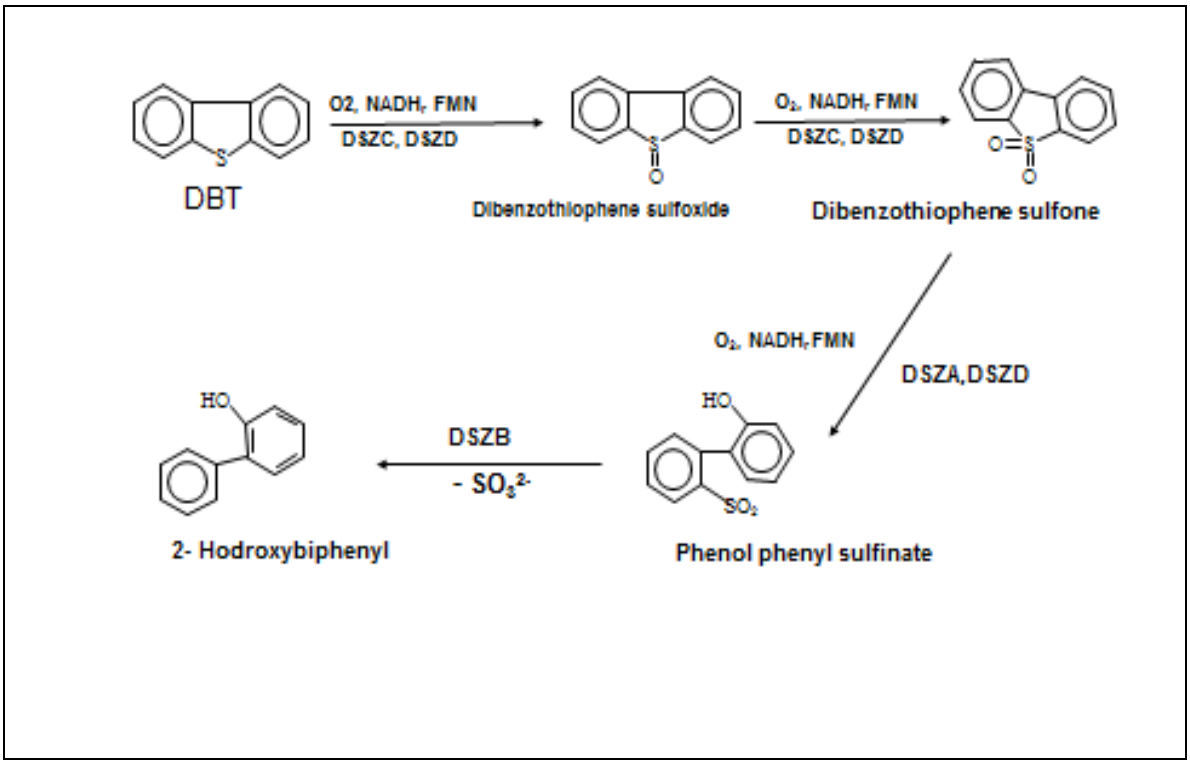


Figure 12. Biodesulfurization pathway of DBT

2.7.6 Desulfurization using porous membrane assisted

Porous membrane has been proposed as promising alternative method for removing undesirable impurities such as sulfur, nitrogen and mercury containing compounds from fuel oils. It has been reported in many publications that membrane separation process involves selective transport of a target compounds and leaving behind the feed. There are two common membrane processes first one known as per-vaporation processes which depends on pressure as a driving and the second known as per-straction processes which depends on concentration gradients across the membrane. The key factor for impurities separation using membrane separation is the hydrophobic and hydrophilic process. Xing reported that the membrane process was used to remove sulfur compounds of refinery products [71].

Saxton investigated the sulfur compounds removal from hydrocarbons fractions (naphtha) using membrane. This method was carried out under pervaporation conditions. Organic solvent (methanol) was used as a transport agent in this process [72].

It was reported that membrane methods required extensive energy consumption to support passing the materials through the membrane. In addition some membrane desulfurization processes required gaseous phase to enhance the permeate rate. It was reported the transport agent is also required in membrane processes to enhance the transport rate of sulfur compounds [73]. Furthermore, In 2006, electro-membrane extraction (EME) was introduced by Pedersen-Bjergaard and Rasmussen as a rapid sample preparation technique based on the the same principle as electrodialysis and electrochemical membrane processes where electrical potential brings about electrokinetic migration of charged species from donor (sample phase) to an acceptor

phase [74]. This method operates on the principle of electrokinetic separation in combination with technical set-up of hollow fiber liquid-phase microextraction (HF-LPME) [75]. EME has the potential for overcoming some of the problems encountered in conventional liquid-liquid extraction (LLE) techniques: high consumption of organic solvents, difficulty in automation and lack of flexibility with regard to extraction chemistry. Also, EME has displayed an improved speed over LPME that's driven by passive diffusion [76]. Electrokinetic migration can occur in both two-phase and three phase systems. In a two phase system, analyte ions move from one liquid phase into another separated by an interface, with one electrode in contact with each phase [77]. Under the influence of applied potential, charged species traverse this interface from one phase to the other as witnessed under electrodyalisis. On the other hand, EME process involves a third phase in the form of an impregnated polymeric material as a supported liquid membrane (SLM) in which the acceptor solution is placed [78]. Polypropylene membrane is commonly used to produce hollow fiber support base for SLM [79]. Gjelstad has explained a mathematical model for EME, and a modified Nernst-Planck equation in combination with Poisson's could be used to describe physico-chemical phenomena controlling the flux of ions over an SLM. Several parameters that control the optimal performance of EME include pH of both donor and acceptor solutions, type of support electrolyte, stirring rate, extraction time and the type of organic solvent used for preparing the SLM [80]. To avoid a memory or carry over effect which can reduce the efficiency of transfer across an SLM into the acceptor phase, a washing cycle should be performed after each extraction [81]. This can be done by flushing both the donor and acceptor channels with impregnating and acceptor solutions respectively. Initially, only

very high voltages were used for EME. Following efforts geared at downscaling EME, miniaturized forms have now been built and electrical fields as small as 3V of DC sources can be used to drive the electrokinetic migration process. A chip format has recently been introduced which displayed high extraction recovery after less than 4s (3µl/min) contact time [82]. Early applications of this EME technique were centered around extraction of peptides and charged drugs from various bio-matrices including whole blood and plasma. These applications have been extended to the extraction and determination of Pb^{2+} from amniotic fluid, blood serum, lipstick and urine matrices. In this procedure, 2-cm of hollow fiber membrane (HFM) with one end heat-sealed was used. The tip of syringe barrel was inserted in the other end. Both the lumen of the HFM and the syringe needle assembly were filled with phosphoric acid /sodium tetraborate buffer (pH 8.1) [83]. The HFM was then dipped into toluene for 2 min to impregnate its wall pores. Platinum wires were used as electrodes, with the positive end dipped into the sample solution while the negative end was connected to the syringe needle assembly, with entire portion of the HFM immersed in the sample solution. These electrodes were supplied with 300V from a DC power supply and the sample solution was agitated at 700rpm for 15 min. Under these conditions, Pb^{2+} ions migrated toward the negative electrode into the HFM containing the acceptor solution. On turning off the voltage supply after the 15 min period, contents of the HFM were collected and 50µL of 20mM EDTA was added to complex the analyte ions at pH 3.4. This was then followed by capillary electrophoresis with UV detection. It was reported that this method displayed good linearity (r^2, 0.9935) and extraction recoveries more than 80% could be achieved within a short period. A highly selective EME procedure was developed for the extraction

of chlorophenols in sea water samples, with recoveries of 74% [84]. Only 10V was used to drive the analytes in alkaline pH across 1-octanol-based SLM in a three phase set-up that was coupled to high performance liquid chromatography with UV detection (HPLC-UV). Unlike the forgoing example of EME application for Pb^{2+} ions , placement of the electrodes in this application was reversed because chlorophenols in the alkaline pH of 12 were ionized to negatively-charged species. At neutral pH, Basheer has recently accomplished the simultanous extraction of both acidic and basic pharmaceuticals from waste water using a novel compartmentalized membrane envelope [85].

2.8 Mercury removal from fuel oils

Mercury is another non-hydrocarbon constituent of fossil fuels with deleterious effects. Mercury in complex matrices in fossil fuel carries its own quantification challenge since such matrices must be completely destroyed at high temperatures without the loss of the analyte [86] . Samples of fossil fuel from different fields contain varying amounts of mercury . Won reported that the mercury emissions from gasoline, diesel and liquefied petroleum gas (LPG) ranging between 1.5ng/m^3 and 26.9ng/m^3 for all the three fuel types, and LPG was found to contain the highest original Hg content [88]. Mercury may also cause a lot of other challenges to the environment [87].

Kelly reportred that solid-phase extraction and carbon-based sorbents are the most commonly used for removal of mercury from petrochemicals. This system, however, does not work effectively for all species of mercury. Suspended or colloidal forms (eg., mercuric sulfide) can evade capture by the sorbent beds [32].

To the best of our knowledge, there's no literature on the use of EME supported with volatge for the simultaneous separation of sulfur, nitrogen and mercury from fossil fuel matrices. From our preliminary investigation, we strongly believe that EME has high potential in this direction. This will be a very good alternative to the costly and mostly problem-prone techniques that are presently in use.

CHAPTE3

RESULTS AND CONCLUSION

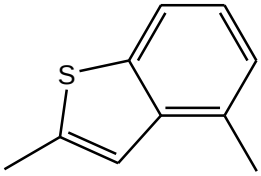
3.1 Materials and instrumentations

3.1.1 Material

High purity nineteen sulfur compounds (Figure 15) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and have been used as model compounds. Various HPLC-grade organic solvents (Figure 13) were purchased from Sigma-Aldrich to study the sulfur compound extraction. A polypropylene hollow fiber and flat sheet membranes were purchased from membrane (Wuppertal, Germany) with the specifications of hollow fiber membrane: inner diameter 0.2μm, wall thickness 200μm and pore size 0.2μm. 15 cm length of HFM was used for extraction. The specifications of flat sheet polypropylene porous membrane :inner diameter 0.2 μm, wall thickness 600μm and pore size 0.2μm. The flat sheet was used in the flow extraction for simultaneous mercury and sulfur removal investigation.

Diesel, Arabian crude oils (light, medium and heavy) have been taken from Ras Tanura refinery, Saudi Arabia. Low sulfur diesel (less than 50 ppm of total sulfur treated by HDS) was taken from Riyadh refinery and organic solvents were purchased from Aldrich.

3.1.2 Sulfur compounds standards



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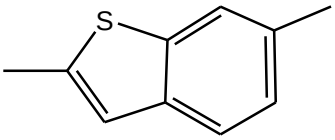

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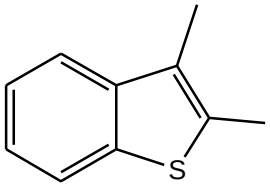

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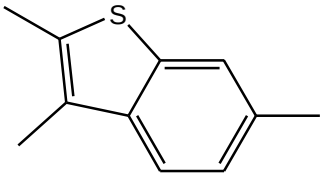
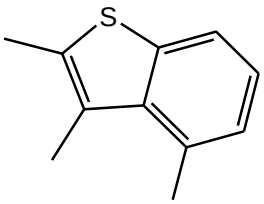
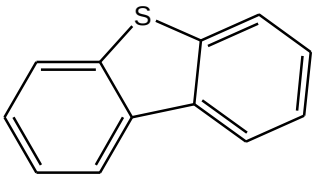


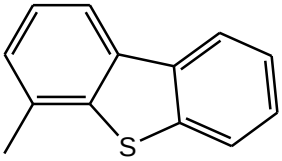
2,3,6 trimethylbenzothiophene



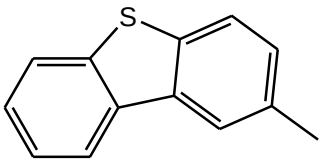
2,3,4 trimethylbenzothiophene



Dibenzothiophene



4-methyl dibenzothiophene



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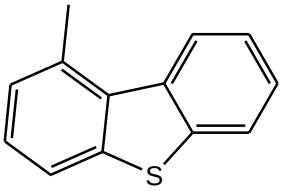

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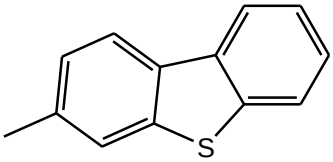
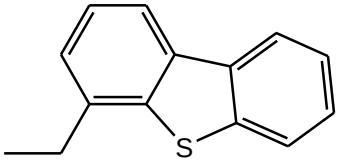


3-methyl dibenzothiophene



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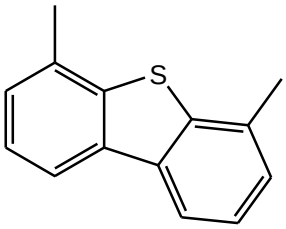

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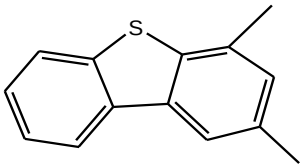

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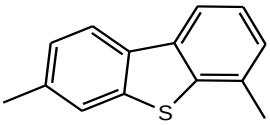
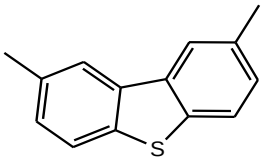
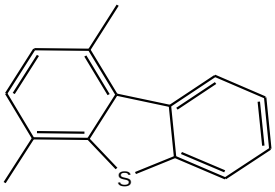


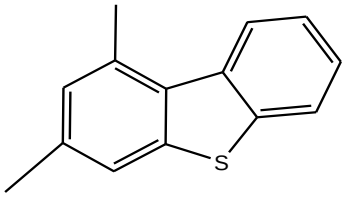
3,6 dimethyl dibenzothiophene



2,8 dimethyl dibenzothiophene



1,4 dimethyl dibenzothiophene



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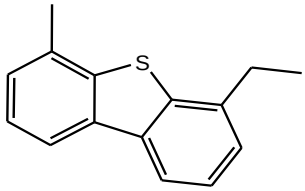
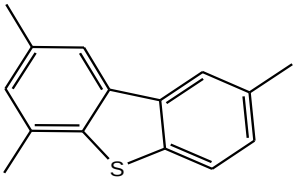


4-ethyl 6-methyl dibenzothiophene

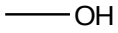
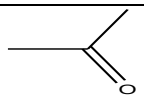
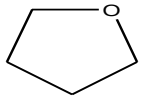
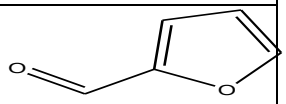
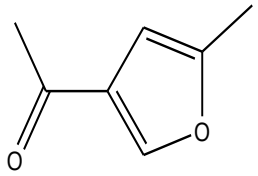
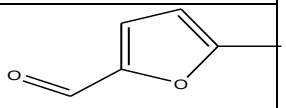
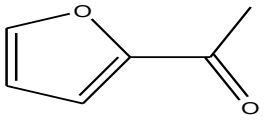


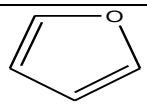
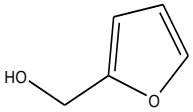
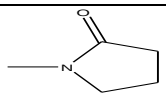
2,4,8 trimethyldibenzothiophene

Figure 13: Target analytes sulfur compounds with their structures

3.1.3 Organic Solvents

Table 10: Organic solvents used as extractive solvents for removal of sulfur compounds

Organic solvent name	**Formula**	**Molecular Weight (g/mol)**	**Structure**
Dodecane	$C_{12}H_{26}$	170.34	
Methanol	CH_3OH	32.04 g/mol	
Acetone	CH_3COCH_3	58.08	
Tetrahydrofuran	C_4H_8O	72.11	
Furfural	$C_5H_4O_2$	96.0	
2-Acetyl 5-Methylfuran	$C_7H_8O_2$	124.14	
Methyl furfural	$C_6H_6O_2$	110.11	
2-Furyl methyl ketone	$C_6H_6O_2$	110.11	

Furan	C_4H_4O	68.08	
Furfuryl alcohol	C_5H_6O2	98.10	
N-Methyl Pyrrolidone	C_5H_9NO	99.0	

3.2 Instrumentations

3.2.1 Gas chromatograph equipped with sulfur chemiluminescence detector (GC-SCD)

The gas chromatography equipped with sulfur chemiluminescence detector is a selective instrument for the analysis of sulfur compounds. In the SCD. detection, reaction between ozone and sulfur compounds form sulfur monoxide (SO) by combustion of the analyte, as described in the following reaction:

$$SO + O_3 \longrightarrow SO_2 + O_2$$

SCD is instrument connected to a vacuum pump that pulls the combustion products at low pressure into a reaction cell, where excess ozone is added. The sulfur dioxide and oxygen produced from this reaction are filtered and detected with a blue-sensitive photomultiplier tube. This instrument has been fully used to measure sulfur containing compounds real diesel and crude oils before and after each treatment. The GC-SCD configurations (type of column, injector temperature, injector flow, sample volume, ramping temperature, gases flow and detector temperature) have been optimized based on sulfur compounds resolutions, as shown in Table 11. Standards and samples were run using the set GC-SCD conditions to obtain well resolved separation (Table11). Figure 14-15 show nineteen sulfur compounds chromatogram with their retention time. Peak identification and retention time were listed in the Table 12.

Table 11: GC-SCD conditions for analyzing sulfur compounds

Chromatography	HP 6890 equipped with FID/SCD and auto injector
Column	DB-1 , 60 meter, 250µm ID , film thickness .025 µm film
Carrier gas	He, constant flow ,1.3 ml/min
Oven	Initial temp 40°C hold 1 minute and ramp temperature at 5 °C/min to 300°C hold for 10 minutes
Injector	250°C, pressure 23.30 psi, total flow 17 ml/min, split ratio 10, split flow 13 ml/min
Injection	1µL
Detector	SCD combination: SCD furnace 800°C, H_2 40 ml /min, air 5-6 ml/min, pressure 300-420 mbar
Integration	Chemstation method parameter with operator check

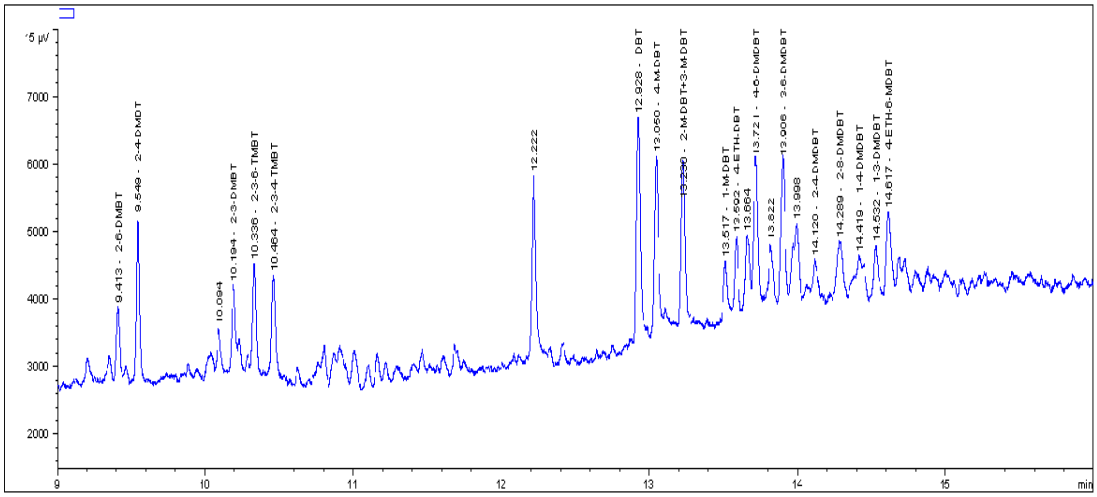


Figure 14: GC-SCD chromatogram of target analyte in crude oils

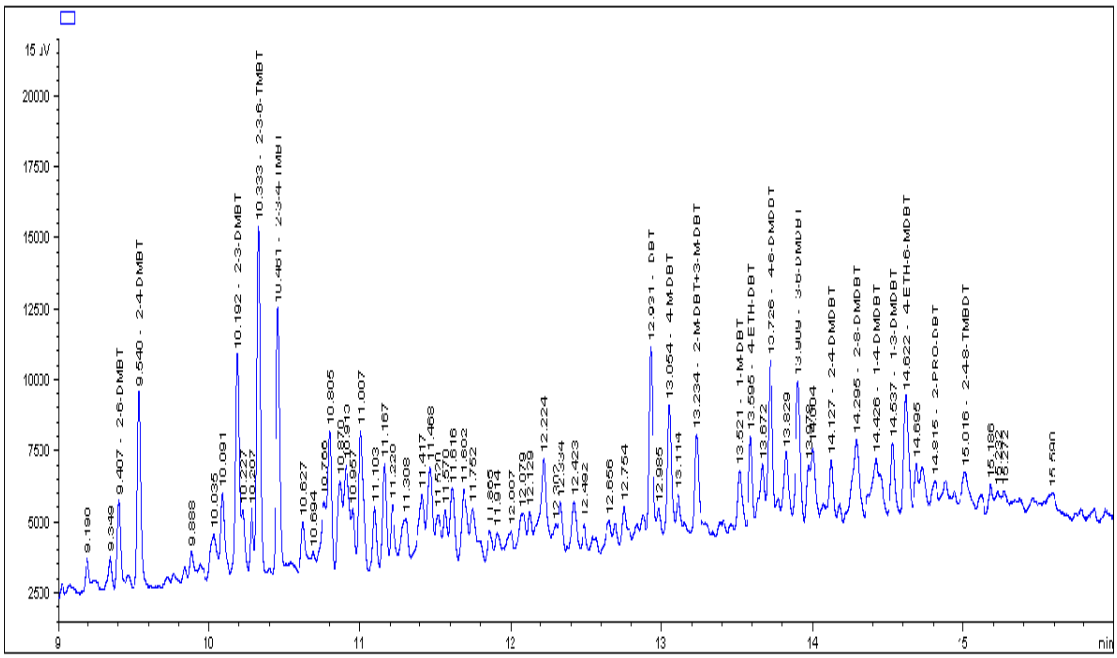


Figure 15: GC-SCD chromatogram of target analyte in diesel

Table 12: Target Analytes with their retention times

No	Target Analytes	RT
1	2,6 DMBT	9.649
2	2,4 DMBT	9.709
3	2,3 DMBT	9.847
4	2,3,6TMBT	10.806
5	2,3,4 TMBT	11.371
6	DBT	12.578
7	4MDBT	13.321
8	2MDBT + 3MDBT	13.449
9	1MDBT	13.626
10	4ET DBT	13.942
11	4,6 DMDBT	14.018
12	2,4 DMDBT	14.104
13	3,6 DMDBT	14.158
14	2,8 DMDBT	14.266
15	1,4 DMDBT	14.337
16	1,3DMDBT	14.582
17	4ET 6 M DBT	14.759
18	2 Prop DBT	14.936
19	2,4,8TMDBT	14.99

3.2.2 Total Sulfur Measurement Using X-ray Fluorescence (XRF)

XRF method is applicable for the determination of sulfur in crude oils and liquid petroleum products. It is applicable for sulfur measurement in the range of 17-46000 ppm. The XRF instrument is calibrated with pure di-n-butyl sulfide standards prepared in sulfur-free oil (e.g. mineral oil) or solvent (toluene) with a range of 0.01-5.0 wt %. The sample cell has to be filled up to the mark (~ 5 grams) and placed in the beam emitted from an X-ray tube. The sulfur element in the sample will be irradiated by primary X-ray, immediately the fluorescence X-ray of sulfur element is generated. The intensity of the fluorescence emission depends on the element concentration in the sample. The excited sulfur radiation is measured and accumulated count (intensity) is compare with counts prepared by calibration standard.

3.2.3 Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT- ICR MS)

3.2.4 Sample preparation

A stock solution was prepared using 50 mg of the oil or diesel sample dissolved in 5 mL toluene. The stock solution was further diluted to a final dilution of 1:5,000 (wt/v) in toluene.

3.2.5 Mass Spectrometry

A 9.4 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer with various ionization modes has been used to acquire mass spectra of the sample. Mass calibration was performed on an Apollo (II) ion source in positive electrospray ionization (ESI) mode. The Apollo (II) ion source is used in the positive Atmospheric Pressure Photo Ionization (APPI) mode for sample measurement. Accumulated molecular ions enter a quadrupole (Q1) which is used to transmit only specific m/z ranges, as a mass analyzer. Then, the ions released from Q1 are accumulated in a hexapole collision cell (h2) before the ion package was injected into the ICR cell for high resolution, high accuracy mass measurement.

3.2.6 Ionization

The APPI is used for sample ionization, the diluted samples were infused via syringe pump at a flow rate of 20 µL/min. Gas flow rates were set at 3 L/min. APPI furnace temperature was set at 350 °C and drying temperature was set to 200 °C. Capillary: 1.5 kV, spray shield: 1.0 kV, capillary exit: 270 V have been set for the relevant ion source potentials.

3.2.7 External and Internal Mass Calibration:

5 mMolar sodium formate solution prepared in water/methanol 1:1 (v/v) is used for external mass calibration in positive mode ESI. Benzothiophenes and alkylated benzenes are used to perform a internal mass calibration for each sample.

3.2.8 Data Processing

FT-ICR MS raw data files were processed using Data Analysis for peak picking with signal to noise ratio (S/N) of 5. The mass calibration of selected signals is affirmed manually. The mass lists of all slices were combined into a single mass list. Then, the mass lists were processed using composer software. Elemental composition assignments are confirmed by the 34sulfur isotopic.

3.3 Experimental

3.3.1 Target sulfur compounds identification in real diesel and crude oils

Diesel contains ultra low sulfur compounds has been injected into GC-CSD to confirm the absence of sulfur containing compounds and the target analytes in diluted diesel was identified, as shown in the Figure 16.

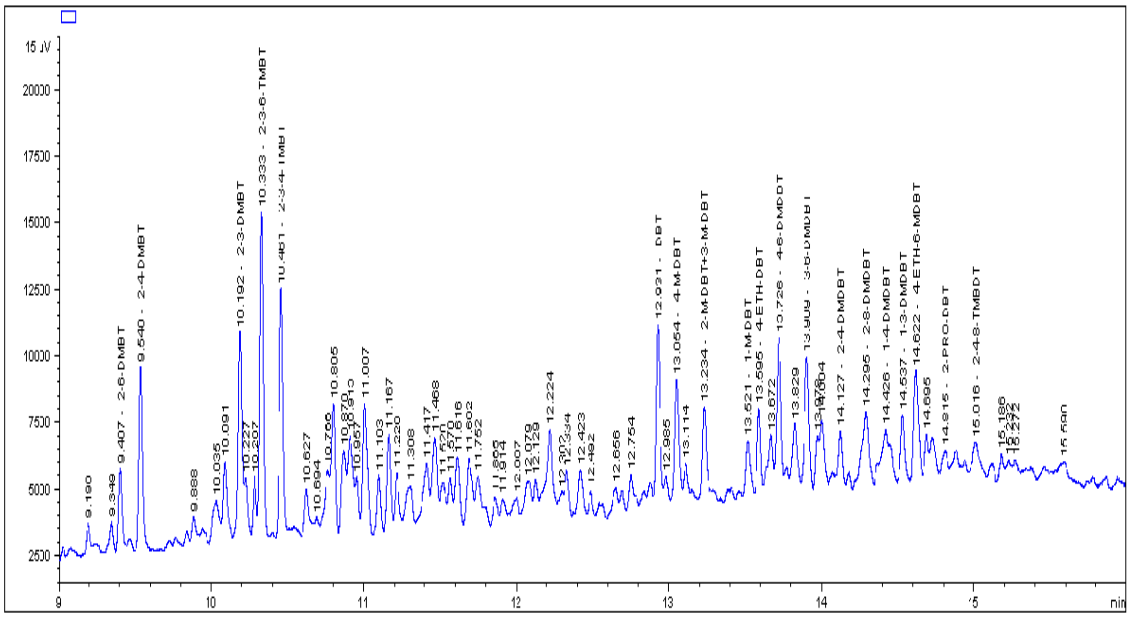


Figure 16: G-SCD Chromatogram of sulfur compounds in diluted diesel

3.3.2 Identify and measure sulfur compounds in diesel and crude oils

The target sulfur containing compounds in real diesel and Arabian crude oils (AH,AM AL) have been identified and measured their concentration using GC-SCD, as shown in Figure 17-19. The diesel and crude oils have been diluted with diesel (low sulfur), 1: 10 ratio. Known standards of sulfur containing compounds have also been used to measure the individual sulfur containing compounds in diesel and crude oils, as listed in Table 13-14.The final concentration of each individual sulfur compound in diesel and crude oils has been multiplied by dilution factor (10).

Table 13: Concentration of target sulfur compounds in diesel.

No	Sulfur compounds in diesel	Concentration (mg/L)
1	2,6 DMBT	40
2	2,4 DMBT	280
3	2,3 DMBT	630
4	2,3,6TMBT	890
5	2,3,4 TMBT	420
6	DBT	620
7	4MDBT	770
8	2MDBT + 3MDBT	600
9	1MDBT	320
10	4ET DBT	160
11	4,6 DMDBT	460
12	2,4 DMDBT	200
13	3,6 DMDBT	810
14	2,8 DMDBT	280
15	1,4 DMDBT	670
16	1,3DMDBT	140
17	4ET 6 M DBT	240
18	2 Prop DBT	120
19	2,4,8TMDBT	190

Table 14: Concentrations of sulfur species in Arabian crude oil (AL, AM and AH)

Sulfur compounds	**AL crude oil (mg/L)**	**AM crude oil. (mg/L)**	**AH crude oil (mg/L)**
2,6 DMBT	15	28	40
2,4 DMBT	60	84	105
2,3 DMBT	12	21	38
2,3,6TMBT	140	205	260
2,3,4 TMBT	70	101	145
DBT	107	144	210
4MDBT	260	298	315
2MDBT + 3MDBT	210	246	276
1MDBT	180	223	280
4ET DBT	90	114	164
4,6 DMDBT	180	242	280
2,4 DMDBT	172	205	245
3,6 DMDBT	310	390	496
2,8 DMDBT	210	233	276
1,4 DMDBT	280	310	384
1,3DMDBT	75	109	135
4ET 6 M DBT	180	210	260
2 Prop DBT	80	105	142
2,4,8TMDBT	45	85	140

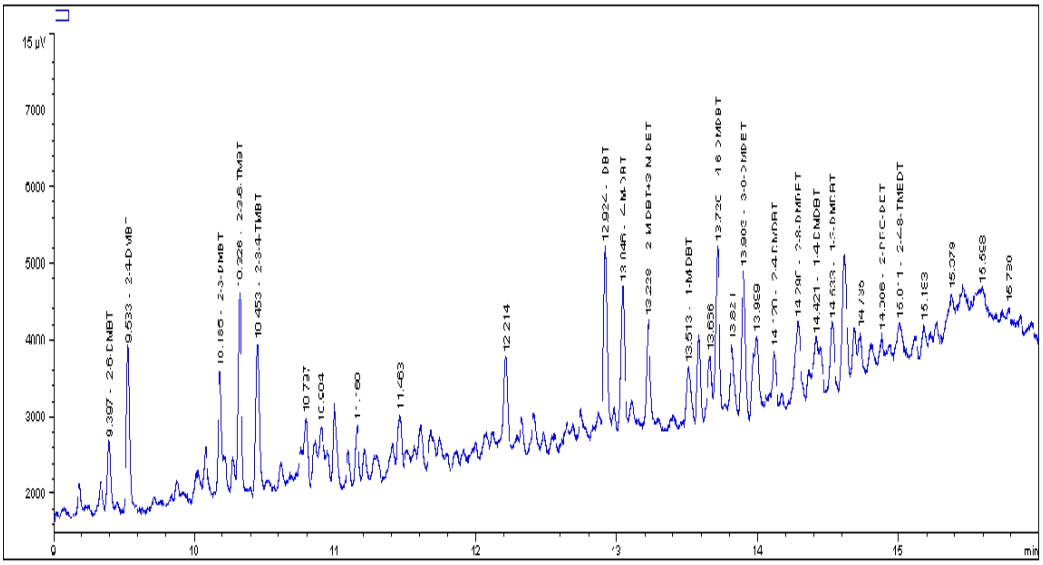


Figure 17: GC-SCD chromatogram of target sulfur species in Arabian light crude oil

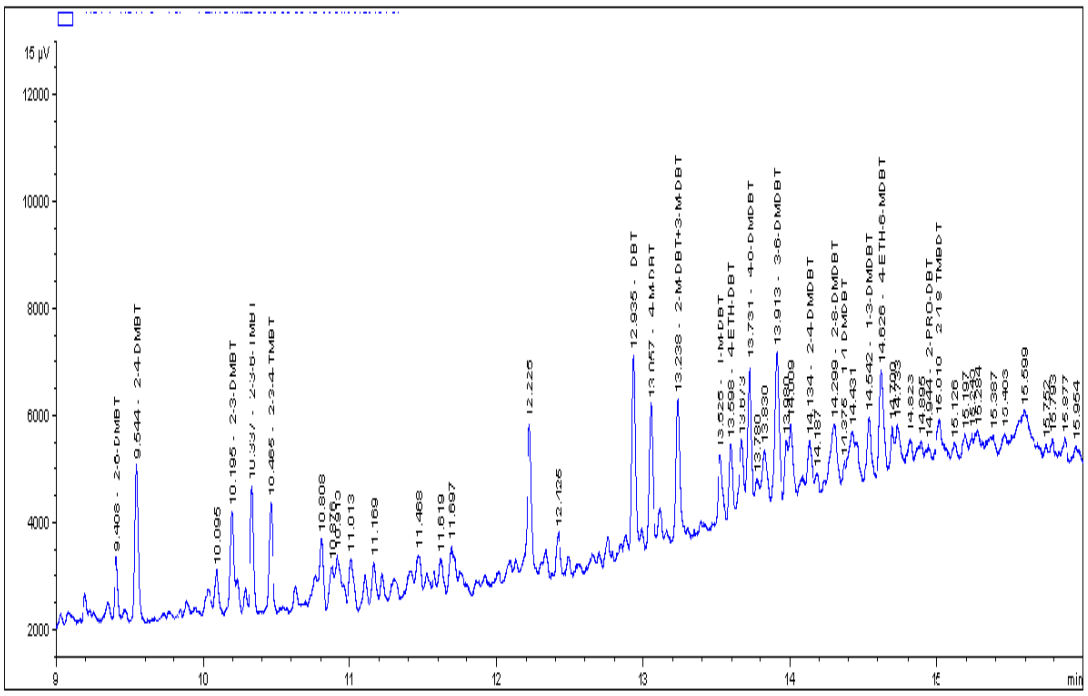


Figure 18: GC-SCD chromatogram of target sulfur species in Arabian medium crude oil

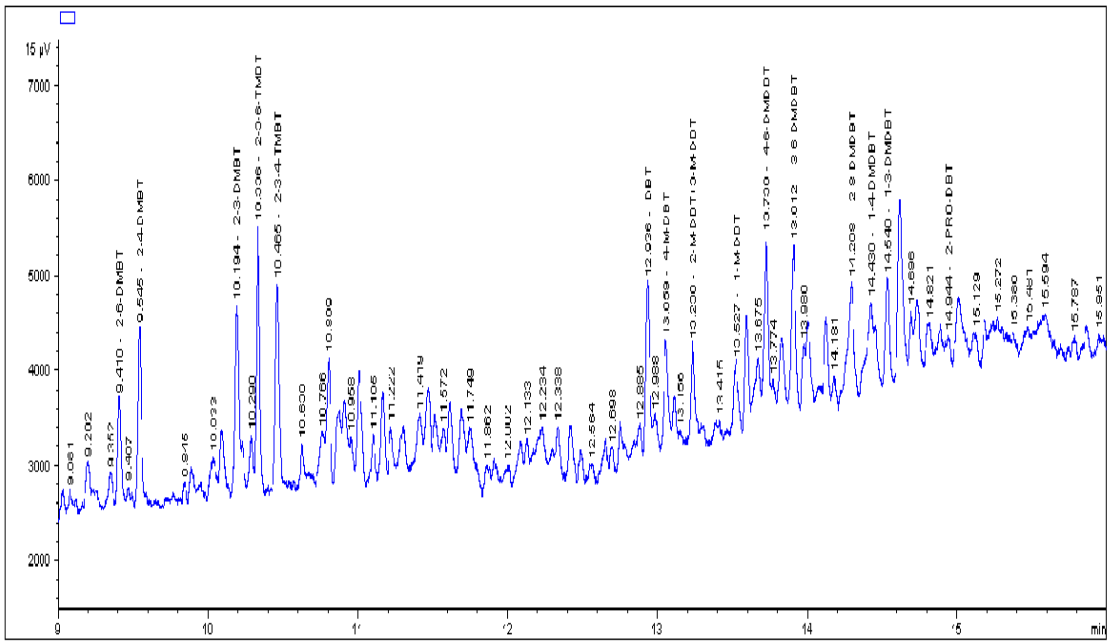


Figure 19: GC-SCD chromatogram of target sulfur species in Arabian heavy crude oil (AH)

3.4 Determination of sulfur compounds concentration in crude oils and fractions using liquid phase micro-extraction supported with hallow fiber membrane (LPME-HFM).

3.4.1 LPME-HFM experiment

LPME supported by a hallow fiber membrane (HFM) has been successfully used to extract analytes (lead) from various matrices. HFM-LPME is a rapid method has been evaluated for removal of sulfur containing compounds for the first time. The LPME experiment was conducted using clean a 10 ml syringe. Prior to each extraction, the syringe was rinsed with acetone and then toluene. 100 µl of organic solvents (indicated in Table 10) were drawn into the syringe. Then, syringe needle was then tightly fitted into HFM, and then organic solvents were added into HFM. HFM with solvent immersed 5mm below the surface of a 4 ml diesel and crude oils in a vials for a period of time (20 minutes).This experiment was conducted at room temperature and atmospheric pressure. The syringe plunger and HFM with organic solvent were depressed so that the extraction takes place between the sample solution and the immiscible solvent in the HFM. After extraction, the stirrer was switched off and the solvent in the HFM was removed into the syringe. Finally, the extracted solvent (1 ml) was injected into the GC–SCD for sulfur species determination. Crude oils and diesel were diluted with low diesel prior to the extraction and dilution factor was taken in consideration.

3.4.2 LPME principle

In LPME, as like liquid–liquid extraction, the analytes of interest are extracted from the samples (donor solution) into smaller volumes (100 µl) of organic solvents (acceptor solution) present inside the porous hollow fibers. Schematic of HFM-LPME is shown in Figure 20. The porous membrane acting as protection layer for organic solvents and avoid any big molecules/ particles extract in the acceptor phase. Simply acting as filtration devise only clean analytes will transport in to the acceptor phase.

A schematic setup of LPME is shown in Figure 22.

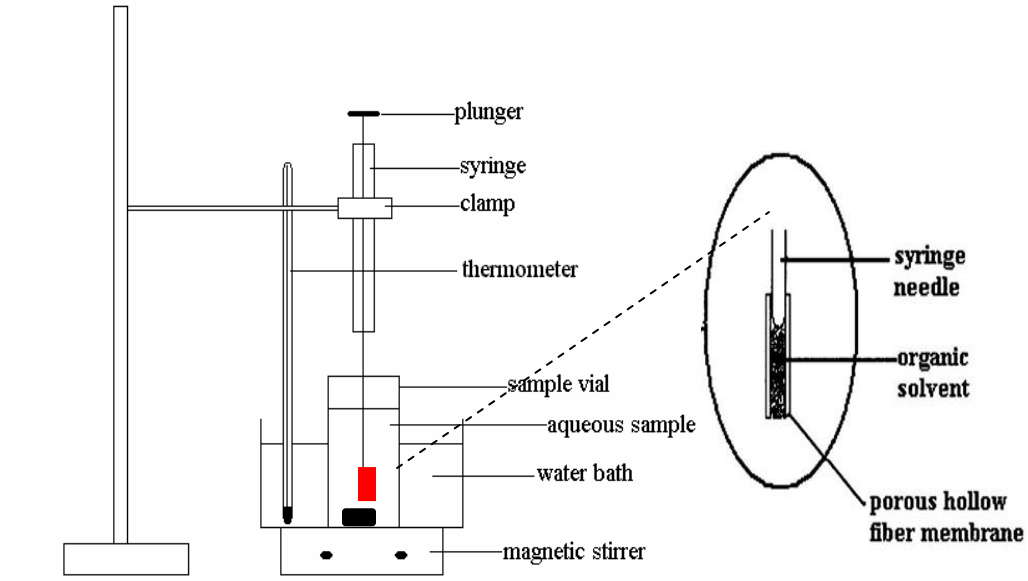


Figure 20: LPME extraction process

3.4.3 Selection of organic solvent

In this study, several polar organic solvents, indicated in Table 10, were evaluated for sulfur compounds extraction. Solvents selection is important for HFM-LPME process; therefore the selection of solvents were considered based on sulfur compounds high capacity, selectivity, high thermal stability and non-toxic.

3.4.4 LPME –HFM

The LPME-HFM showed that this method has high potential to be used as alternative method for determination sulfur containing compounds in petroleum products. Thus, the optimum conditions of this method have been evaluated as follows:

3.4.5 Organic solvents evaluation for sulfur compounds removal

Several organic solvents (Table 15) have been evaluated for sulfur compounds removal from real diesel and crude oils. The results revealed that n-methyl pyrrolidone demonstrated good selectivity for all target analytes (nineteen sulfur compounds) and no significant solvent loss during extraction as well as was the given the highest total sulfur recovery. Whereas, the rest of organic solvents give less selectivity for sulfur compounds recovery compare to n-methyl pyrrolidone along with LPME- HFM, as shown in Table 15-16. The order of organic solvents selectivity for sulfur compounds recovery as follows: n-methylpyrrolidone> furfural >dodecane> 2 acetyl 5-methyl furan > 5-methyl furfural> acetone >furfural alcohol, as shown Figure 21-22

Table 15: Removal of sulfur compounds using LPME –HFM with various organic solvents

Sulfur Compounds	Furfural	N-methypyrrolidone	Furfural alcohol
2,6 DMBT	380	446	209
2,4 DMBT	1100	1153	515
2,3 DMBT	500	597	131
2,3,6TMBT	750	876	440
2,3,4 TMBT	278	316	147
DBT	2657	2991	541
4MDBT	2200	2450	593
2MDBT + 3MDBT	2300	2440	578
1MDBT	1610	1500	346
4ET DBT	950	1000	217
4,6 DMDBT	1700	1881	367
2,4 DMDBT	700	817	195
3,6 DMDBT	1100	1170	350
2,8 DMDBT	900	1095	120
1,4 DMDBT	897	1000	375
Total sulfur area	18022	19732	5124

Table 16: Removal of sulfur compounds using LPME –HFM with various organic solvents

Sulfur Compounds	Acetone	dodcane	2-acety 5-methyl furan	5- methyl furfural
2,6 DMBT	280	350	120	217
2,4 DMBT	859	1000	1000	1050
2,3 DMBT	215	440	250	120
2,3,6TMBT	709	850	650	300
2,3,4 TMBT	297	300	270	340
DBT	651	600	181	390
4MDBT	635	2000	1700	1800
2MDBT + 3MDBT	671	1360	2000	2000
1MDBT	394	1330	1600	1400
4ET DBT	256	900	850	930
4,6 DMDBT	403	700	1300	1500
2,4 DMDBT	630	640	700	650
3,6 DMDBT	100	860	900	800
2,8 DMDBT	100	1240	590	900
1,4 DMDBT	150	1100	1000	620
Total sulfur area	6350	13670	13111	13017

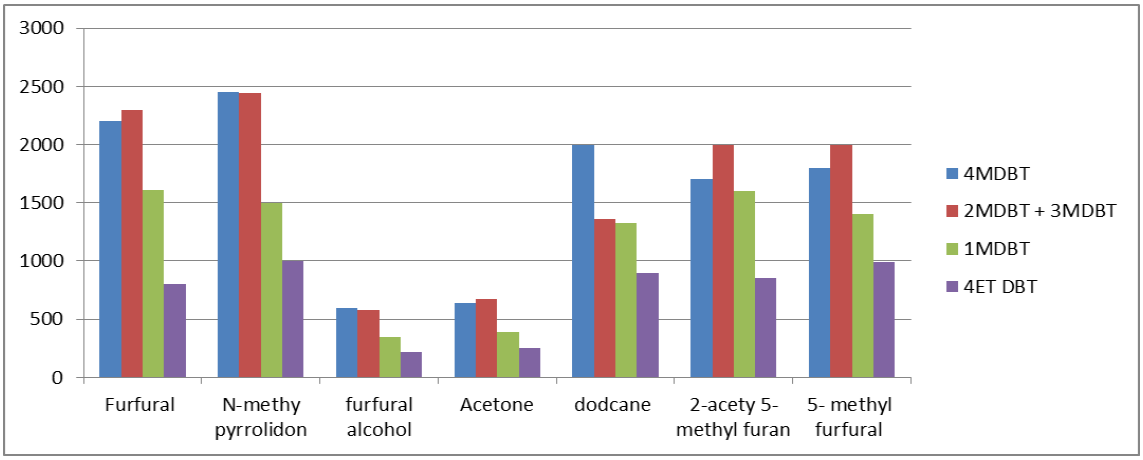


Figure 21: Removal of sulfur compounds using LPME-HFM with various organic solvents, used as extractive solvents

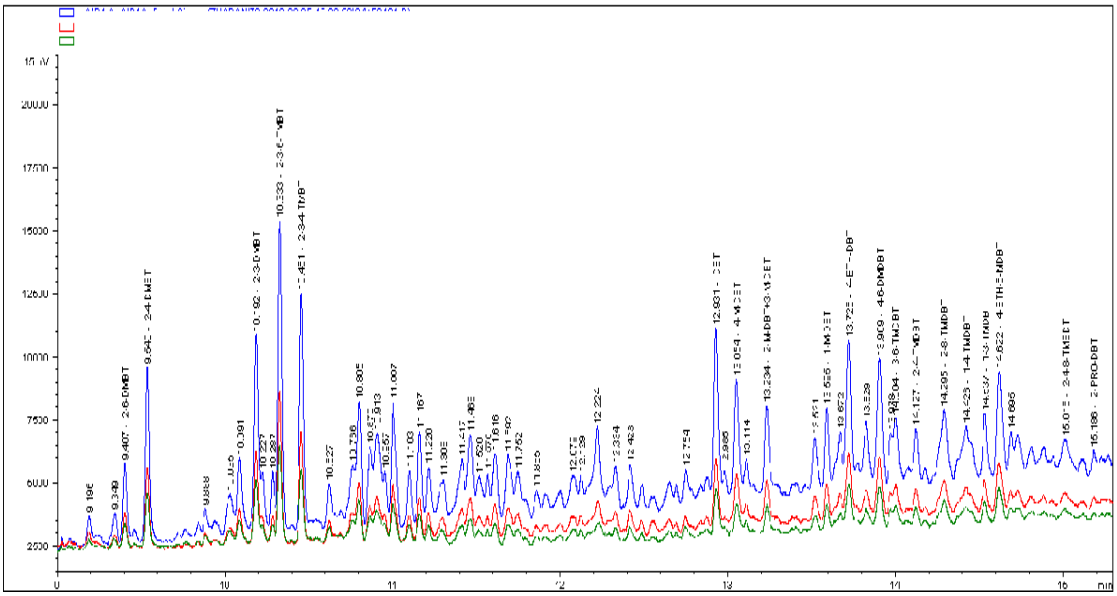


Figure 22: Comparison between organic solvents, blue target analytes removal with n-methyl pyrrolidone, red extracted with furfural alcohol and green with acetone

3.5 LPME optimum extraction time

The LPME extraction times of sulfur compounds recovery were investigated at 5, 10, 15, 20, 30 and 60 minutes on the diesel sample extracted with organic solvent n-methyl pyrrolidone as well as furfural. The total sulfur area of all target analytes components have been calculated and the results showed that the optimum extraction time was reached at 20 minutes of contact between the samples and organic solvents. The total sulfur content began to stabilize and slightly decreased after 20 minutes, as shown in Table 17 and Figure 23.

Table 17: Evaluating the LPME –HFM optimum extraction time

Time minutes	LPME-HFM methyl pyrrolidone (solvent) Total sulfur area	LPME-HFM Furfural (solvent) Total sulfur area
5	3221	1100
10	3311	2050
20	6474	2800
30	4524	2100
60	3541	2050

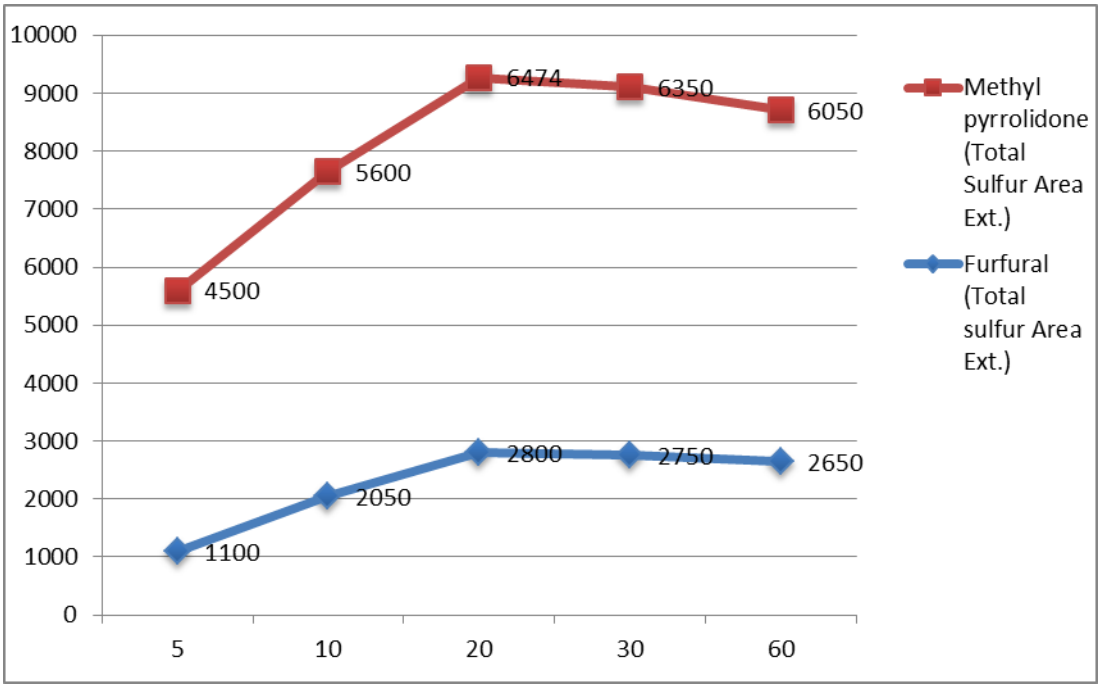


Figure 23. Evaluating the LPME- HFM optimum extraction time, using n-methyl pyrrolidone and furfural as extractive solvents

3.5.1 Optimum sample: solvent ratio

3.5.3.1 The optimum sample volume: organic solvent ratio has been selected as follows:

A) 1: 1 ratio, sample volume 15 ml and solvent volume 0.18 ml

B) 1:2 ratio, sample volume 15 ml and solvent volume 0.36 ml

C) 1:3 ratio, sample volume 15 ml and solvent volume 0.54 ml

The results showed that the total sulfur area of sulfur components was decreased as the solvent volume increased. The results indicated that 1:1 ratio was given the highest sulfur compounds extraction using n-methyl pyrrolidone along with LPME-HFM followed by 1:2 ratio and the lowest was 1:3 ratio, as shown in Table 18 and Figure 24

Table 18: Study the LPME –HFM optimum ratio sample : solvent

Sulfur components	Sample: Solvent 1:1	Sample: Solvent 1:2	Sample: Solvent 1:3
2,6 DMBT	240	201	195
2,4 DMBT	580	524	400
2,3 DMBT	240	190	140
2,3,6TMBT	483	455	414
2,3,4 TMBT	270	210	170
DBT	1782	1410	1313
4MDBT	1440	1140	1150
2MDBT + 3MDBT	1400	1136	1070
1MDBT	793	604	630
4ET DBT	355	319	360
4,6 DMDBT	236	160	212
2,4 DMDBT	980	865	182
3,6 DMDBT	486	345	370
2,8 DMDBT	790	503	570
1,4 DMDBT	670	511	576
1,3DMDBT	210	180	140
4ET 6 M DBT	270	210	140
2 Prop DBT	257	240	210
2,4,8TMDBT	483	193	344
Total sulfur area	11965	9396	8586

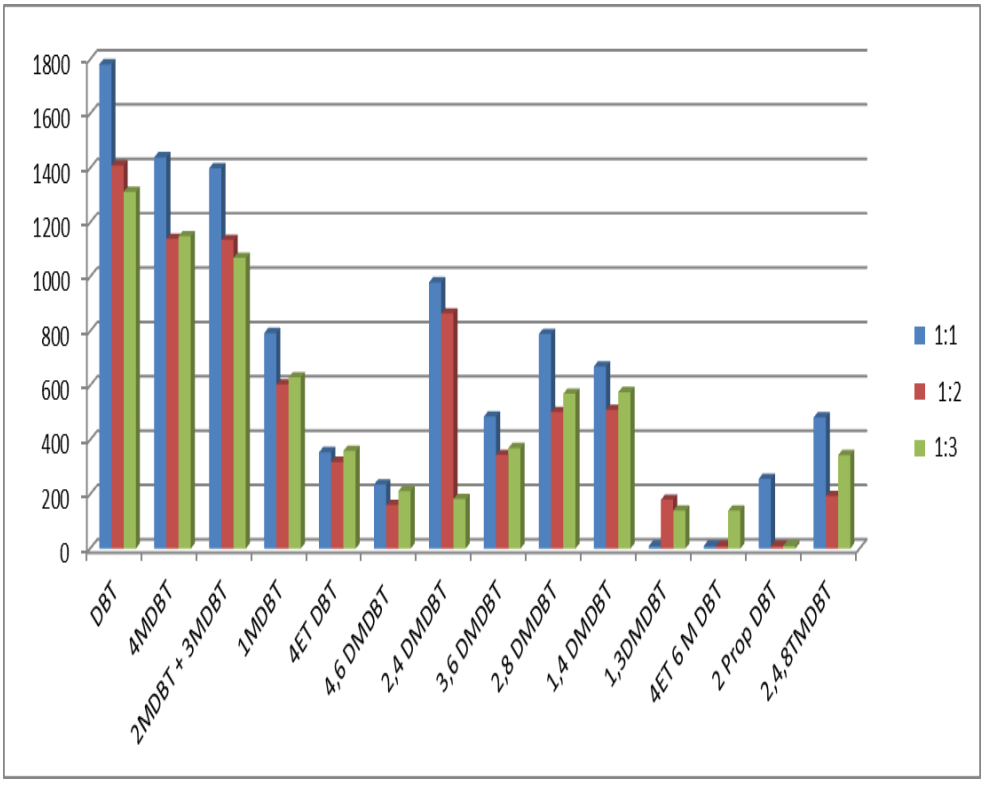


Figure 24: LPME-HFM optimum ratio

3.5.2 Sample volume optimum

The optimum sample volume has also been selected as follows:

A) Samples volume 15 ml and solvent 0.18 ml

B) Sample volume 7.5 ml and solvent 0.18 ml

C) Sample volume 3.5 ml and solvent 0.18 ml

The results displayed that the ratio between sample and solvent (3.5 ml:0.18 ml) was given the highest total sulfur area recovery followed by second ratio (7.5: 0.18 ml) and the lowest was (15 ml : 0.18 ml), as shown in Figure 25.

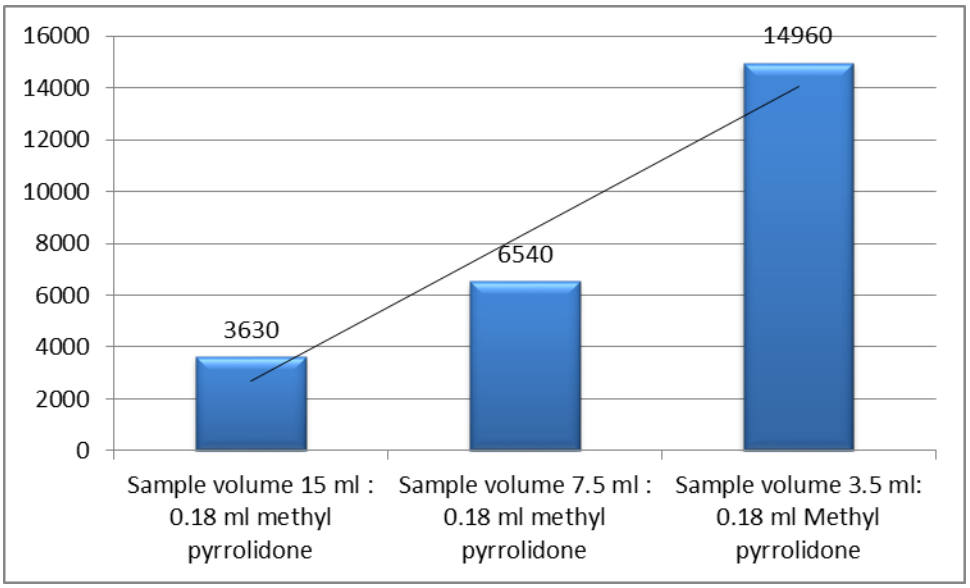


Figure 25: LPME-HFM evaluate optimum ratio

Table 19 : LPME-HFM optimum conditions:

Sample volume	3.5 ml
Solvent volume	0.18 ml
Equilibrium time	20 minutes
HFM length	15 cm

3.6 Quantitative parameters

3.6.1 Linearity evaluation

Linearity of LPME-HFM has been evaluated using the following ratio:

1) 1 ml : 20 ml

2) 1 ml :10 ml

3) 1 ml : 5 ml

4) 1 ml : 2.5 ml

This study was conducted at room temperature and atmospheric pressure. 3.5 ml of each solution (blending) was taken and added into 10 ml beaker. 0.18ml of (n-methyl pyrrolidone) was taken for extraction study. The extraction time was 20 minutes (optimum extraction time). A dynamic linear range of nineteen sulfur compounds were studied and established from (2 - 10 ppm of 2,6-DMBT), (12 - 93 ppm of 2,4-DMBT), (31 – 188 ppm 2,3- DMBT) (28 – 287 ppm of 2,3,6 TMBT from), (23 - 112 ppm of DBT) , (27 – 254 ppm of 4-MDBT from) , (21 - 197 ppm of 2-MDBT + 3-MDBT from), (11 - 102 ppm of 1-MDBT from), (8 -59 ppm of 4-ET-DBT from) , (25 – 237 ppm of 4,6-DMDBT from), (6 - 70 ppm of 2,4- DMDBT from), (36 - 284 ppm of 3,6-DMDBT), (7 – 93 ppm of 2,8-DMDBT) , (33 - 164 ppm of 1,4-DMDBT),(12 - 65 ppm of 1,3-DMDBT) and (8 - 49 ppm 2,4,8-TMDBT) . The results indicated that the LPME-HFM technique is linear with high the correlation factor (R^2) ranging from 0.9966 to 0.9999, as shown in Table 20 and Figure 26.

Table 20 : Linearity Evaluation of the Target Analyst

Sulfur Compounds	1:20 Ratio (µg/ml)	1:10 Ratio (µg/ml)	1:5 Ratio (µg/ml)	1:2.5 Ratio (µg/ml)
2,6 DMBT	18	40	73	97
2,4 DMBT	114	280	503	929
2,3 DMBT	305	630	1222	1880
2,3,6TMBT	283	890	1297	2866
DBT	228	620	1122	408
4MDBT	268	770	1288	2541
2MDBT + 3MDBT	207	600	1049	1974
1MDBT	112	320	542	1016
4ET DBT	78	160	302	591
4,6 DMDBT	248	460	1127	2367
2,4 DMDBT	54	200	372	692
3,6 DMDBT	356	810	1511	2835
2,8 DMDBT	68	280	485	933
1,4 DMDBT	328	670	1381	1640
1,3DMDBT	115	140	315	652
2,4,8TMDBT	77	190	299	486

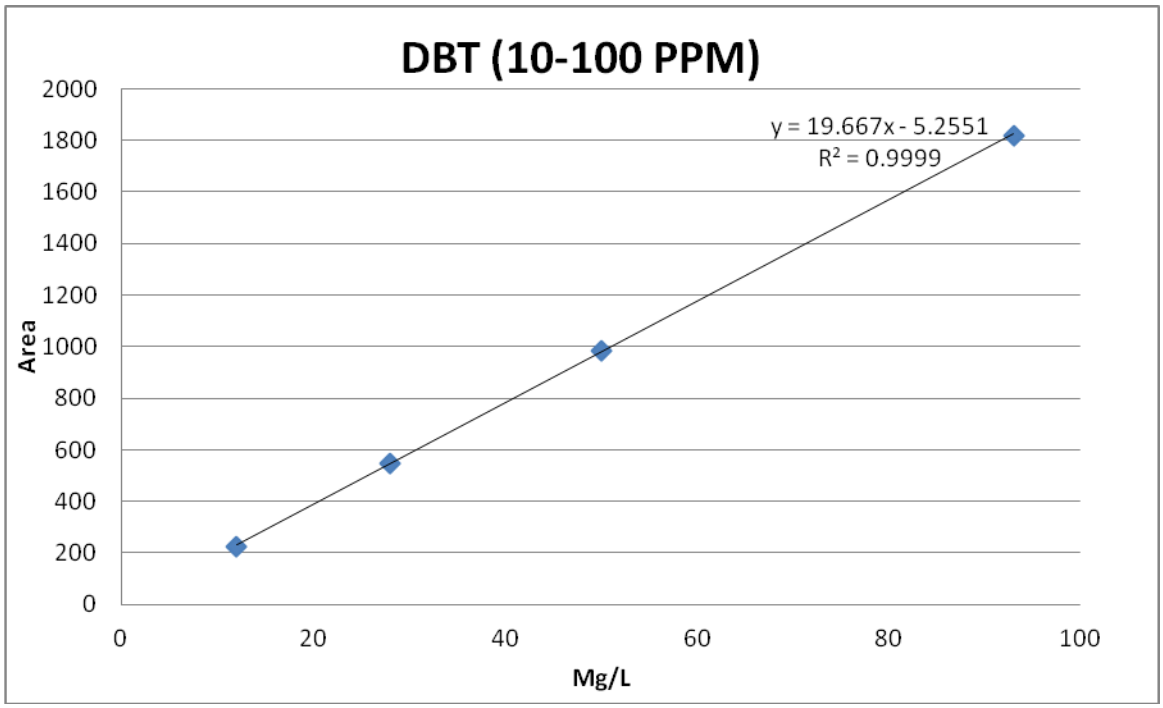


Figure 26: Linearity response of target sulfur compound (DBT)

3.7 Application of LPME-HFM

This technique (LPME-HFM) has been investigated for extract sulfur containing compounds from Arabian crude oils such as Arabian light (AL) Arabian medium (AM), Arabian heavy (AH) and diesel. The results revealed that the method (LPME-HFM) was comparable with ASTM method for determination of sulfur compounds in crude oils and fractions (diesel), as shown in Table 21-23.

Table 21: Determination of individual sulfur species concentration in AL oil.

Sulfur compounds	Sulfur compound conc. using ASTM(mg/L)	Sulfur compounds conc. Using HPME-HPM (mg/L)	Recovery (%)
2,6 DMBT	15	12	80
2,4 DMBT	60	74	123
2,3 DMBT	12	15	125
2,3,6TMBT	140	122	87
2,3,4 TMBT	70	63	90
DBT	107	134	125
4MDBT	260	289	111
2MDBT + 3MDBT	210	228	108
1MDBT	180	188	104
4ET DBT	90	101	112
4,6 DMDBT	180	196	108
2,4 DMDBT	172	199	115
3,6 DMDBT	310	332	107
2,8 DMDBT	210	235	111
1,4 DMDBT	280	290	103
1,3DMDBT	75	86	114
4ET 6 M DBT	180	189	105
2 Prop DBT	80	98	122.5
2,4,8TMDBT	45	51	113

Table 22: Determination of individual sulfur species concentration in AM oil

Sulfur compounds	Determination of conc. present in AM using ASTM (mg/L)	Determination of conc. present in AM using HPME-HPM (mg/L)	Recovery (%)
2,6 DMBT	28	20	71
2,4 DMBT	84	67	80
2,3 DMBT	21	15	73
2,3,6TMBT	205	201	98
2,3,4 TMBT	101	84	83
DBT	144	149	104
4MDBT	298	232	78
2MDBT + 3MDBT	246	173	71
1MDBT	223	201	90
4ET DBT	114	109	96
4,6 DMDBT	242	230	95
2,4 DMDBT	205	155	76
3,6 DMDBT	390	295.	76
2,8 DMDBT	233	245	105
1,4 DMDBT	310	279	90
1,3DMDBT	109	103	95
4ET 6 M DBT	210	173.	82
2 Prop DBT	105	97	92
2,4,8TMDBT	85	63	75

Table 23: Determination of individual sulfur species concentration in AH oil

Sulfur compounds	Sulfur compounds conc. using ASTM (mg/L)	Sulfur compounds conc. using HPME-HPM (mg/L)	Recovery (%)
2,6 DMBT	40	35	88
2,4 DMBT	105	96	91
2,3 DMBT	38	45	118
2,3,6TMBT	260	236	91
2,3,4 TMBT	145	123	85
DBT	210	220	104
4MDBT	315	307	97
2MDBT + 3MDBT	276	250	91
1MDBT	280	215	77
4ET DBT	164	149	91
4,6 DMDBT	280	257	92
2,4 DMDBT	245	237	97
3,6 DMDBT	496	458	92
2,8 DMDBT	276	273	99
1,4 DMDBT	384	258	67
1,3DMDBT	135	113	84
4ET 6 M DBT	260	207	80
2 Prop DBT	142	149	105
2,4,8TMDBT	140	131	94

3.8 Conclusion

The LPME-HPM supported with organic solvent n-methyl pyrrolidone gave promising results for determination of sulfur compounds in crude oils and fractions, with high recovery > 80 %. The results showed that the LPME-HFM technique is linear from 0.5-500 ppm and the correlation factor (r^2) ranging from 0.9966 to 0.9999 with high reproducibility, as shown in Table 20 and Figure 26. Also, the results indicated that the detection limit of this method was 100 ppb. The organic solvent (n-methyl pyrrolidone) was selected due to its structure, the paired electrons on the oxygen have ability to interact with sulfur compounds and hydrogen and form strong bond (O-S or O-H). Also, the solvent has high thermal stability and lower corrosively as compared with to other organic solvents such as (furfural, furan, and 2-acetyl 5-methyl furan).

CHAPTER 4

4.0 Dispersive liquid-liquid microextraction techniques (DLLME) used for sulfur compounds removal from petroleum products

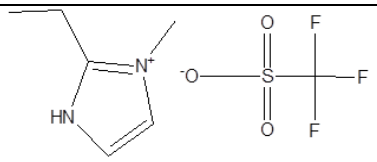
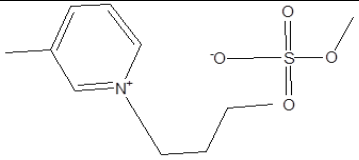
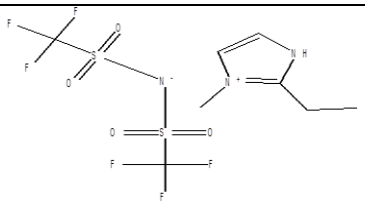
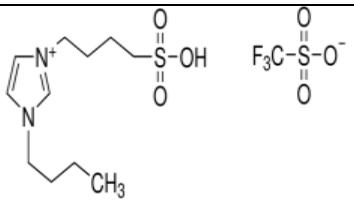
Main objective of this study is to investigate the suitability of ionic liquid in the application of sulfur compounds extraction. For the DLLME, no membrane was used solvent was directly introduced into the sample for removal sulfur compounds from petroleum products. Ionic liquids are eclectically conductive thus suitable ionic liquid could be used for electromembrane extraction study.

4.1 materials

4.1.1 Sulfur compounds, organic solvents, diesel and crude oils samples were described in section 3.1.1

4.1.2 The following ionic liquids have been purchased from Aldrich Company and used for sulfur compounds removal:

Table 24: ionic liquids used as extractive solvents in DLLME

Ionic liquid name	Structure
1-ethyl-3-methylimidazolium tri-fluoromethansulfonate [EMIM][CF_3SO_3]	
butyl 3-methyl pyridiniummethylsulfate [BMPY][CH_3SO_4]	
1- ethyl 3- methyl imidazoliumbis (trifluoromethylsulfonyl) amide [EMIM][$F_3CSO_2]_2N$	
3- butyle 1-imidazoliol 1- butane sulfonicacidtriflate[BIMB][BSATF]	

4. 2 DLLME experiment

4.2.1 DLLME experiment using ILs as extractive solvents

In a 5 ml of diesel known concentration of sulfur compounds was added into 50 ml centrifuge tube and then 200 µl of (IL) was added. Addition of IL gave cloudy solution and the IL acts as dispersive solvent. The solution (diesel and IL) was ultrasonic for 20 minutes. After that, the dispersive solvent was separated from the sample using 5 ml syringe. ILs are not volatile and not suitable for direct injections into gas analysis. Therefore, back extracted with 200 µl of toluene for 2- minutes were performed. The top layer (toluene) was injected to GC-SCD.

4.2.2 DLLME experiment using IL mixed with organic solvent

In this experiment, the IL was mixed with organic solvent (n-methyl pyrrolidone) (1:10 IL: organic solvent) and used as disersive extraction solvent. 5 ml of diesel sample was added into 50 ml centrifuge tube and then 200 µl of IL was added into the centrifuge tube using 5 ml syringe. The solution (diesel and IL) was mixed for 20 minutes then the solvent was separated from the sample. Toluene has been added to the dispersive solvent and mixed for almost 2 minutes to re-extract the sulfur compounds from IL mixture and then the top layer (toluene) was injected to GC-SCD. In addition, the diesel sample was injected into GC-SCD before and after each extraction.

4.2.3 Evaluate the linearity of DLLME experiment

The linearity of the DLLME experiment was evaluated by extracting known concentration of diesel sample by serial dilutions mixture, as follows:

1- 1:1 ratio (low diesel : high diesel)

2- 1:5 ratio (low diesel : high diesel)

3- 1:10 ratio (low diesel: high diesel)

4- 1:20 ratio (low diesel : high diesel:

4.2.4 Evaluate the ultrasonication effect on the DLLME experiment

The ultrasonication technique has been used to enhance the extraction techniques. 5 ml of diesel (1:10 low sulfur: high sulfur) have been added into 50 ml centrifuge tube and then 200 µl of dispersive solvent (1:10 IL : organic solvent n-methyl pyrrolidone) was added. The solution has been mixed for about 5 minutes and then ultrasonicate for two minutes. After that, the centrifuge tube was removed and dispersive solvent was separated. 200 µl of toluene was added to re-extract sulfur compounds prior to GC-SCD injection. The experimental conditions were repeated for different ultrasonic times (5, 10, 15 and 20 minutes).

4.3 Selecting and evaluating ionic liquids for removal of sulfur compounds

Table 25 shows the IL used in this study, and they were selected based their chemical and physical properties. The blank diesel sample (1:10) was extracted with ILs using the procedure (4.2.1) and the results revealed that Ethyl 3-methyl 1- imidazolium, trifluoromethanesulfonate was extracted more sulfur containing compounds followed by Butyl 3- methyl pyridinium, methyl sulfate and 1-Ethyl 3- methyl imidazolium, bis (tri fluoro methyl sulfonyl) amide. However, 3- Butyle 1- imidazoliol, 1- butane sulfonic acid triflate was given the lowest total sulfur extraction due to its viscosity and density were high as compared to the other ILs.

Table 25: Sulfur compounds extraction using DLLME, ILs solvents:

Sulfur compounds	[EMIM][CF3SO3] mg/L	[BMPY][CH3SO4] mg/L
2,6 DMBT	280	210
2,4 DMBT	230	150
2,3 DMBT	980	750
2,3,6TMBT	1420	950
DBT	180	120
4MDBT	250	220
2MDBT + 3MDBT	580	420
1MDBT	210	180
4ET DBT	630	530
4,6 DMDBT	780	340
2,4 DMDBT	396	260
3,6 DMDBT	890	540
2,8 DMDBT	340	420
1,4 DMDBT	560	490
1,3DMDBT	450	420
2,4,8TMDBT	450	180
2-PRO-DBT	270	320
Total Area	8896	6500

Table 26: Sulfur compounds extraction using DLLME, ILs used as solvents:

Sulfur compounds	[EMIM][F3CSO2]2N mg/L	[BIM][BSATF] mg/L
2,6 DMBT	140	80
2,4 DMBT	210	105
2,3 DMBT	320	270
2,3,6TMBT	540	390
DBT	290	100
4MDBT	205	130
2MDBT + 3MDBT	350	250
1MDBT	160	170
4ET DBT	580	650
4,6 DMDBT	270	140
2,4 DMDBT	240	210
3,6 DMDBT	660	230
2,8 DMDBT	310	280
1,4 DMDBT	370	170
1,3DMDBT	250	160
2,4,8TMDBT	280	120
2-PRO-DBT	240	80
Total Area	5415	3535

4.3.1 Combination of ionic liquid with organic solvents using (1:10) ratio

The total sulfur compounds recovery using pure ILs as dispersive solvent was very low. However, to overcome this issue the dispersive solvents (ILs) have been diluted by organic solvents (n-methyl pyrrolidone) using 1:10 ratio and the experiment using section 4.2.2 conditions. The results showed that the IL [BIM][BSATF] was less efficient than [EMIM][F_3CSO_2]$_2$N, [BMPY][CH3SO4] and [EMIM][CF_3SO_3] for sulfur compounds recovery, as shown in Table 26-27 and Figure 27.

Table 27: Target sulfur compounds extraction using DLLME

Sulfur compounds	[EMIM][CF3SO3] combined with n-methyl pyrrolidone	[BMPY][CH3SO4] combined with n-methylpyrrolidone
2,6 DMBT	558	460
2,4 DMBT	340	319
2,3 DMBT	1173	830
2,3,6TMBT	1249	1132
DBT	1124	1158
4MDBT	271	284
2MDBT + 3MDBT	339	270
1MDBT	458	357
4ET DBT	364	257
4,6 DMDBT	1237	1210
2,4 DMDBT	372	650
3,6 DMDBT	590	450
2,8 DMDBT	467	327
1,4 DMDBT	673	472
1,3DMDBT	1530	1280
2,4,8TMDBT	450	650
2-PRO-DBT	880	750
Total Area	12075	10856

Table 28: Target analytes extraction using DLLME. ILs combined with organic solvent used as extractive solvent.

Sulfur compounds	[EMIM][F3CSO2]2N Combined with n-methyl pyrrolidone	[BIM][BSATF] Combined with methyl pyrrolidone
2,6 DMBT	370	275
2,4 DMBT	269	178
2,3 DMBT	655	598
2,3,6TMBT	712	687
DBT	816	723
4MDBT	275	194
2MDBT + 3MDBT	198	217
1MDBT	267	248
4ET DBT	291	191
4,6 DMDBT	890	679
2,4 DMDBT	212	210
3,6 DMDBT	380	290
2,8 DMDBT	310	285
1,4 DMDBT	428	368
1,3DMDBT	890	754
2,4,8TMDBT	212	460
2-PRO-DBT	520	334
Total Area	7695	6691

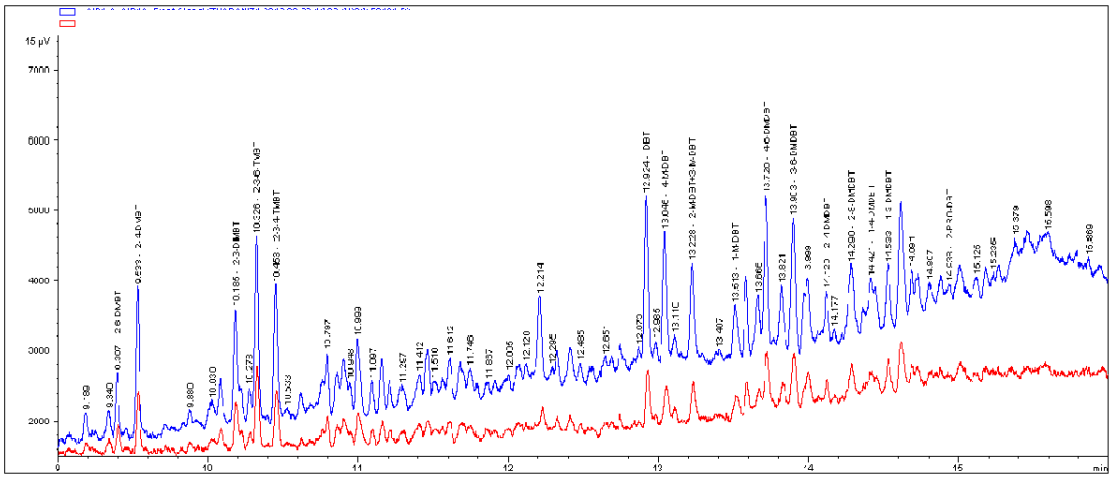


Figure 27: GC-SCD chromatogram of target analytes using DLLME.

IL alone (in green red) IL combined with organic solvent (in blue).

4.3.2 Sulfur removal using IL[EMIM][CF_3SO_3] combined with methyl pyrrolidone at various ultrasonication time

In this study, the total sulfur compounds recovery, using DLLME experiment 4.2.3, was increased by using ultrasonic techniques. The results showed that the total sulfur area was increased by 44% from 12075 to 21800 at optimum time, as shown in Table 28. In addition, the optimum time for ultrasonication was studied and the results revealed that the optimum time for ultrasonic has been reached at 10 minutes and after that the total sulfur area recovery is steady, as indicated in Table 28 and Figure 28.

Table 29: DLLME target analytes extraction using IL combined with organic solvent and ultrasonication

Sulfur compounds	(2 min) ultrasonication	(5 min) ultrasonication	(10 min) ultrasonication	(15 min) ultrasonication	(20 min) ultrasonication
2-6- DMBT	430	418	530	750	740
2-4- DMBT	423	386	332	457	458
2-3- DMBT	570	684	450	797	380
2-3-6-TMBT	670	864	1124	1045	212
2-3-4-TMBT	1350	1507	790	1180	1270
DBT	760	856	1200	550	633
4-M-DBT	728	870	774	690	624
2-M-DBT+ 3-M-DBT	432	870	2420	4360	3980
1-M-DBT	113	915	864	1127	1180
4-ETH-DBT	652	356	423	442	519
4-6-DMDBT	1300	2323	2140	2890	2750
2-4-TMDBT	466	334	450	313	520
3-6-TMDBT	870	1033	2780	1661	1780
1-4-TMDBT	450	560	1280	890	1302
1-3-TMDBT	980	1296	2114	1780	1700
4-ETH--6-MDBT	596	650	1240	550	1370
2-PRO-DBT	1450	1880	1290	600	800
2-4-8- TMDBT	1250	1500	1600	1630	1650
Total	13490	17302	21801	21712	21868

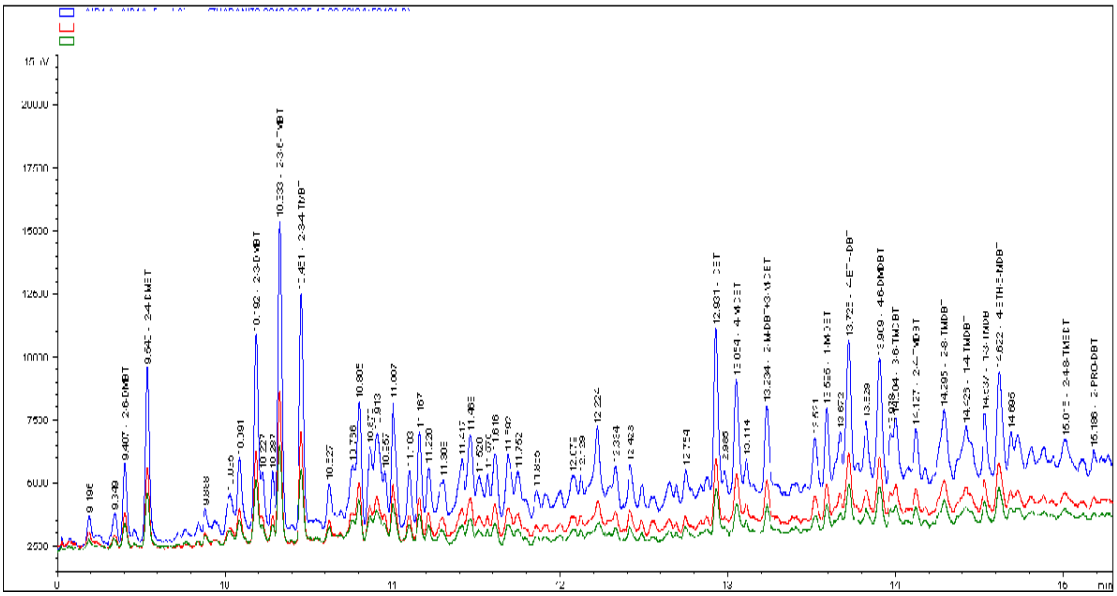


Figure 28 : GC-SCD chromatogram of target analytes extraction using DLLME.

IL solvent (in green) chromatogram, IL combined with organic solvent (in red) and IL combined with organic solvent and ultrasonication (in blue)

4.4 Application of DLLME techniques

Application of DLLME was tested for the preconcentration for sulfur compounds.

The DLLME is suitable for petroleum products such as kerosene, diesel and naphtha. However, this method is not applicable for crude oils samples. This is due to high solubility of the dispersive solvent in crude oils. This method was also successfully applied for the removal of low and high sulfur compounds concentration from petroleum product diesel ranges from 18-1500 mg/L. Moreover, the dynamic linearity of DLLME method has been evaluated using different diesel ratio such as 1:5, 1:10 and 1:20 (high sulfur diesel: low sulfur diesel). The results showed that this method is linear with high correlation (R^2) ranges from 0.9976 to 0.9999.

Conclusion:

The DLLME may also be considered as a promising technique for the pre concentration removal of sulfur compounds in diesel, kerosene, naphtha and gasoline. The results revealed that IL [EMIM][CF_3SO_3] combined with organic solvent (n-methyl pyrrolidone) in presence of ultrasonication give high sulfur compounds recovery. Moreover, this method was linear with high correlation factor ranged from 0.9967-0.09998. However, this method is slower than LPME-HFM and less sulfur compounds recovery.

CHAPTER 5

5.0 Removal of sulfur compounds using electro-membrane assisted flow reactor

The results obtained from LPME –HFM was promising for removal of sulfur compounds in crude oils and fractions (Chapter 3). For the first time, the LPME-HFM was scaled up to simultaneous removal of sulfur, nitrogen and mercury from crude oils using a porous membrane assisted flow reactor. The possibility of using porous membrane assisted flow reactor for desulfurization, denitrogenation and mercury removal form crude oil fractions was investigated. In this chapter various extraction solvents were again investigated. The solvents (furfural, methyl pyrrolidone and ILs [EMIM][CF_3SO_3] and [BMPY][CH_3SO_4]) were selected for experiment optimization. These solvents (organic and ILs) gave better performance in LPME-HFM and DLLME methods. The porous membrane assisted flow reactor parameters such as ratio of IL with organic solvent (1:10), feed flow, extraction time and voltage were optimized.

5.1 Material and chemicals

Organic solvents (furfural, methyl furfural and n-methyl pyrrolidone) and ionic liquids ([EMIM][CF_3SO_3] and [BMPY][CH_3SO_4]) used for the simultaneous sulfur removal were described in chapter 4. A polypropylene flat sheet membranes purchased from membrane (Wuppertal, Germany) with the specifications inner diameter 90.60 μm, the porosity in the range of 0.35-0.70 μm. The feed crude oils and fractions have been obtained from RasTanura Refinery before desulfurization process. A reactor membrane cell has been modified and consist of three compartments, two for feed and one for extractive solvent, as shown in Figure 29.

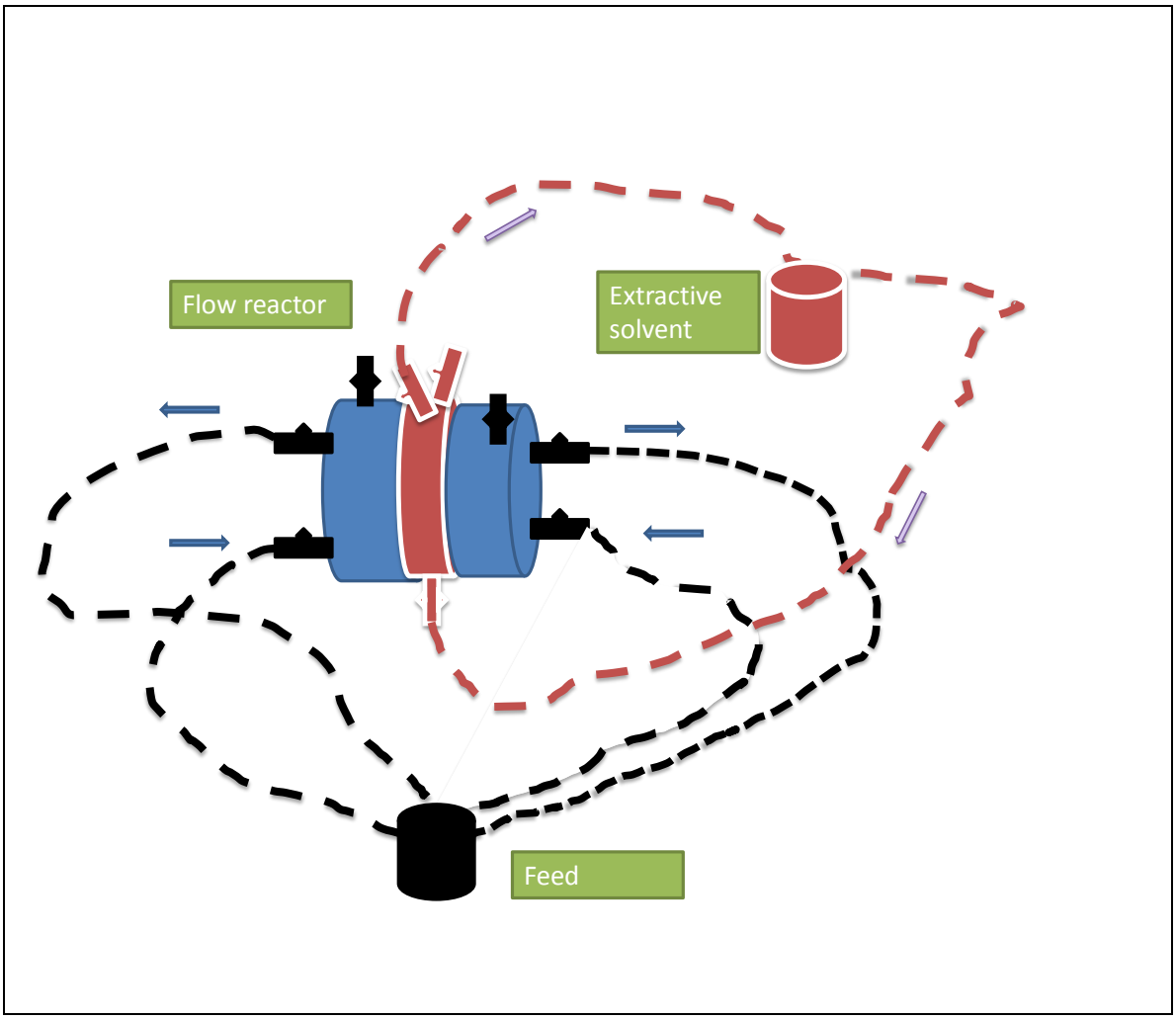


Figure 29 : Porous membrane assisted flow reactor diagram

5.2 Simultaneous removal of sulfur compounds

5.2.1 Sulfur compounds removal using porous membrane assisted flow reactor with extractive solvents

1- Ionic liquid used as extractive solvent

100 ml of feed (diesel) with known concentration of sulfur compounds was taken into 150 ml closed container. In the first extraction, seven milliliter of immiscible ILs [EMIM][CF_3SO_3]has been added into the solvent compartment. Also, another IL [BMPY][CH_3SO_4] has been evaluated. Two membranes were fixed in membrane contactor (sandwiched between two compartments), as shown in Figure 29. Each IL was examined for removal of sulfur compounds. The feed (crude oils or diesel) was fed on both side of the cell and circulate in closed loop. The circulation speed was examined at different rates 10, 20 and 35 rpm. Two liquids (feed and solvent) are not mixing, but get contact within the membrane pores and then feed impurities such as nitrogen, sulfur and mercury compounds pass vis the membrane pores into the solvent. The solvent's efficiency for impurities removal has been tested during 5, 10, 15, 20 and 30 minutes. The IL samples have been re-extracted with toluene prior to GC-SCD injection.

2- Organic solvents used as extractive solvents

The close flow membrane reactor setup experiment was investigated to extract impurities (sulfur and nitrogen compounds as well as mercury) from oils and petroleum products using high polarity organic solvents (furfural, methyl furfural and n-methyl pyrrolidone) as extractive solvent. The extraction efficiency of the organic solvents was compared with ILs.

Typical procedure has been conducted for both extractive solvents IL and organic solvents.

3- Combination of IL with organic solvents, as extraction solvents

This experiment setup and procedure have also been examined for impurities (sulfur and nitrogen compounds) removal using organic solvent combined with IL (1:10 ratio) as extractive solvent. The appropriate conditions of porous membrane flow reactor experiment such as pump rate, extraction time, extraction time and ratio of IL with organic solvents were optimized.

5.3 Results and discussion

5.3.1 Removal of sulfur compounds using PMAFR; various solvents

In this study, removal of nineteen target sulfur compounds from diesel was investigated. Two ILs [EMIM][CF_3SO_3] and[BMPY][CH_3SO_4] have been examined at ambient conditions. These two ionic liquids were selected before on the previous based DLLME experiments (chapter 4).

The results demonstrated that the percentage of sulfur compounds extraction increases with increasing extraction times, as shown in Figure 30. The results revealed that the percentage removal of total sulfur increased from 3.0 to 8.0% during the recycling times between 5 and 20 minutes, respectively. After 20 minutes the extraction reach the optimum extraction time using [EMIM][CF_3SO_3].Whereas, the total percentage removal of sulfur compounds increased from 2 to 6 % with the extraction recycling times between 5 and 20 minutes using [BMPY][CH_3SO_4], as shown in Table 30-31. This is indication that the [EMIM][CF_3SO_3] has ability to extract more sulfur compounds than[BMPY][CH_3SO_4].

Table 30: Removal of sulfur compounds using porous membrane assisted with [EMIM][CF_3SO_3] used as extractive solvent at various extraction times.

Sulfur compounds	5 minutes mg/L	10 minutes mg/L	15 minutes mg/L	20 minutes mg/L	30 minutes mg/L
2-6 DMBT	0.8	1.3	1.7	2.0	1.9
2-4-DMBT	6.4	8.5	8.1	15.7	11.2
2-3-DMBT	14.0	24.8	38.6	53.2	39.6
2-3-6 TMBT	20.2	28.7	15.5	15.1	14.2
2-3-4TMBT	3.4	5.2	6.3	9.7	9.6
DBT	11.3	26.0	38.8	46.7	38.5
4-MDBT	28.5	55.8	73.0	95.8	81.8
2-MDBT+3MDBT	23.3	44.8	75.1	92.9	74.9
1-MDBT	8.7	25.7	31.0	42.6	37.0
4-ETH -DBT	3.3	4.1	6.1	6.0	5.1
4-6 DMDBT	15.2	24.3	13.0	48.6	35.7
3-6 DMDBT	4.7	18.5	25.4	52.3	36.4
2-4 DMDBT	13.1	33.8	36.8	48.5	36.8
2-8 DMDBT	10.8	13.5	15.9	16.8	15.0
1-4 DMDBT	20.3	26.7	41.6	60.5	58.7
1-3 DMDBT	7.1	11.0	12.7	14.2	13.3
4-ETH -6-MDBT	6.0	7.0	6.9	17.4	7.8
2-PRO-DBT	13.3	17.1	23.5	27.1	25.0
2-4-8 TMDBT	8.0	10.13	12.3	18.2	18.8

Table 31: Simultaneous removal of sulfur compounds using porous membrane assisted flow reactor, [BMPY][CH_3SO_4] used as extraction solvent at various extraction times.

Sulfur compounds	5 minutes mg/L	10 minutes mg/L	15 minutes mg/L	20 minutes mg/L	30 minutes mg/L
2-6 DMBT	0.8	1.0	1.2	1.8	1.8
2-4-DMBT	3.9	5.8	6.7	10.2	9.8
2-3-DMBT	12.2	19.4	29.8	34.3	30.1
2-3-6 TMBT	7.3	16.3	15.5	21.7	20.7
2-3-4TMBT	3.6	4.1	4.9	8.2	7.6
DBT	8.2	16.2	23.6	36.8	30.9
4-MDBT	24.2	40.3	56.9	65.0	60.0
2-MDBT+3MDBT	21.1	34.5	46.0	55.5	49.8
1-MDBT	7.2	17.8	25.5	28.3	26.0
4-ETH -DBT	2.5	4.6	5.5	5.7	4.6
4-6 DMDBT	8.0	20.9	27.5	31.1	28.6
3-6 DMDBT	4.3	13.6	19.6	41.3	25.5
2-4 DMDBT	8.1	23.7	26.7	38.5	21.7
2-8 DMDBT	10.4	14.9	14.7	15.4	13.6
1-4 DMDBT	16.2	24.7	36.8	57.8	48.6
1-3 DMDBT	5.7	9.8	11.8	12.8	7.3
4-ETH -6-MDBT	4.6	5.7	6.4	16.0	7.3
2-PRO-DBT	11.8	16.4	24.8	25.9	21.2
2-4-8 TMDBT	9.1	8.0	11.3	13.7	12.9

5.3.2 Membrane assisted flow reactor using organic solvents as extraction solvent

In this study, flow reactor was used to investigate the various organic solvents such as furfural, methyl furfural and n-methyl pyrrolidone in a larger volume sample size (100 ml). The objective of this study is to select the desirable organic solvent and to compare it with ionic liquids extraction efficiency. The results showed that the percentage removal of sulfur compounds increased to 4.5 to 5 and to 6 to 7 %, using the methyl furfural. The extraction efficiency increased along with the recycling times 5, 10, 15 and 20 minutes. After 20 minutes, the extraction reaches the optimum time. In addition, the percentage removal of sulfur compounds increased long with extraction time using furfural as extractive solvent. The percentage removal increased to 5 to 8 % along with extraction time from 5 to 20 minutes, respectively. The extraction efficiency increased from 5 to 10 % along with increasing extraction time from 5 to 20 minutes, respectively.

The results indicated that the n-methyl pyrrolidone extracted more sulfur compounds followed by furfural and then methyl furfural, as shown in Table 32-34.

Table 32: Removal of sulfur compounds using porous membrane assisted with methyl furfural as extraction solvent at various extraction times.

Sulfur compounds	5minutes mg/L	10 minutes mg/L	15 minutes mg/L	20 minutes mg/L	30 minutes mg/l
2-6 DMBT	1.0	1.9	2.1	2.4	2.6
2-4-DMBT	9.7	12.4	13.5	15.7	13.6
2-3-DMBT	23.1	24.8	26.0	28.4	27.5
2-3-6 TMBT	28.3	30.1	30.8	32.3	31.4
2-3-4TMBT	6.2	7.5	7.7	9.6	9.6
DBT	15.7	16.9	19.1	21.0	20.1
4-MDBT	63.3	65.8	71.2	87.5	72.5
2-MDBT+3MDBT	33.5	46.0	64.1	80.4	65.1
1-MDBT	29.0	32.3	34.3	38.9	40.9
4-ETH -DBT	4.1	4.8	6.4	7.9	6.8
4-6 DMDBT	19.5	25.0	26.1	46.7	31.5
3-6 DMDBT	25.5	26.0	29.3	37.0	36.4
2-4 DMDBT	30.7	34.3	35.8	43.9	32.3
2-8 DMDBT	15.5	18.1	21.5	22.8	21.5
1-4 DMDBT	27.0	26.7	37.0	41.6	37.8
1-3 DMDBT	12.8	14.3	15.8	17.0	17.0
4-ETH -6-MDBT	7.6	8.7	9.5	15.2	15.7
2-PRO-DBT	27.1	30.7	33.6	40.0	40.7
2-4-8 TMDBT	12.3	14.7	17.4	23.9	23.9

Table 33: Removal of sulfur compounds using porous membrane assisted with furfural as extraction solvent at various times.

Sulfur compounds	5minutes mg/L	10 minutes mg/L	15 minutes mg/L	20 minutes mg/L	30 minutes mg/L
2-6 DMBT	1.5	2.3	2.8	2.8	2.9
2-4-DMBT	9.1	9.4	13.6	15.0	15.7
2-3-DMBT	23.1	29.7	41.7	37.2	36.4
2-3-6 TMBT	23.8	28.3	27.9	35.0	30.6
2-3-4TMBT	6.4	6.0	6.0	15.1	13.9
DBT	18.2	26.0	37.8	36.6	34.9
4-MDBT	56.7	59.2	86.7	105.0	97.5
2-MDBT+3MDBT	35.9	54.6	79.5	99.6	88.8
1-MDBT	27.7	27.0	37.6	40.9	44.8
4-ETH -DBT	4.6	5.4	5.7	7.5	8.2
4-6 DMDBT	21.4	26.4	29.0	42.7	38.7
3-6 DMDBT	18.5	20.1	26.1	31.0	41.8
2-4 DMDBT	33.8	37.3	41.8	52.4	46.4
2-8 DMDBT	16.8	21.5	22.2	21.5	22.8
1-4 DMDBT	35.4	42.4	47.8	60.9	49.3
1-3 DMDBT	15.8	18.8	22.8	27.7	31.9
4-ETH -6-MDBT	7.9	9.8	11.1	14.4	17.1
2-PRO-DBT	21.4	28.6	30.0	30.0	42.1
2-4-8 TMDBT	13.8	12.3	15.4	22.0	29.5

Table 34: Removal of sulfur compounds using porous membrane assisted with n-methylpyrrolidone as extractive solvent at various times.

Sulfur compounds	5 minutes mg/L	10 minutesmg/L	15 minutesmg/L	20 minutesmg/L	30 minutesmg/L
2-6 DMBT	1.9	2.7	3.1	3.3	3.4
2-4-DMBT	9.6	10.5	15.8	16.1	15.9
2-3-DMBT	25.4	43.9	64.1	71.4	67.4
2-3-6 TMBT	26.1	30.6	33.6	37.2	32.8
2-3-4TMBT	5.5	5.0	6.3	17.0	14.7
DBT	22.1	34.4	58.4	67.2	62.4
4-MDBT	61.7	63.3	108.9	122.5	119.2
2-MDBT+3MDBT	38.3	65.1	100.5	107.2	92.9
1-MDBT	31.0	32.3	41.5	46.8	48.1
4-ETH -DBT	4.9	5.7	7.1	9.3	10.2
4-6 DMDBT	24.6	28.2	31.5	39.5	33.7
3-6 DMDBT	21.2	22.8	27.9	35.3	34.2
2-4 DMDBT	38.3	42.8	45.9	62.0	64.0
2-8 DMDBT	20.3	22.5	27.8	21.5	20.6
1-4 DMDBT	40.8	49.3	60.1	72.4	66.3
1-3 DMDBT	17.5	21.9	25.5	32.2	28.6
4-ETH -6-MDBT	9.9	10.9	11.9	18.7	15.5
2-PRO-DBT	22.3	29.3	34.3	40.0	44.3
2-4-8 TMDBT	9.2	12.1	17.9	24.4	24.1

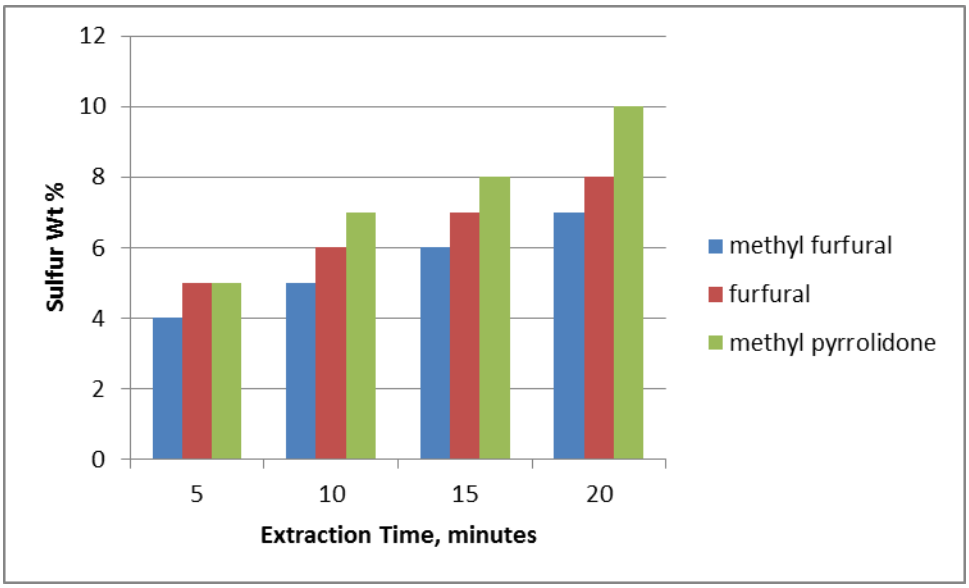


Figure 30: Total sulfur (%) extracted with various organic solvents

5.4 Membrane assisted flow reactor with ionic liquid-solvent combinations

5.4.1 Combination of IL ([EMIM][CF3SO3]) with n-methyl pyrrolidone

To improve the removal of sulfur compounds, combination of IL and organic solvents were used in the flow reactor. A 10 ml of organic solvent (n-methyl pyrrolidone) was combined with 1 ml of IL [EMIM][CF_3SO_3]. The results showed that the percentage removal of sulfur compounds increased to 6, 8, 9 and 11 % during 5, 10, 15 and 20 minutes, respectively, as shown in Table 35 and Figure 31. After 20 minutes the extraction reaches the optimum time.

Table 35: Removal of sulfur compounds using porous membrane assisted using combination of IL with methyl pyrrolidone as extractive solvent.

Sulfur compounds	5 minutes mg/L	10 minutes mg/L	15 minutes mg/L	20 minutes mg/L	30 minutes mg/L
2-6 DMBT	2.7	3.1	3.5	3.7	3.7
2-4-DMBT	11.2	12.6	14.4	16.8	15.0
2-3-DMBT	28.4	47.4	70.1	73.0	70.9
2-3-6 TMBT	24.8	28.3	30.6	32.8	30.1
2-3-4TMBT	8.2	9.9	10.2	11.2	12.6
DBT	32.9	40.8	53.0	73.6	67.8
4-MDBT	73.3	80.0	115.8	127.5	124.2
2-MDBT+3MDBT	50.7	84.3	115.8	124.5	114.7
1-MDBT	33.6	37.6	43.5	52.4	46.1
4-ETH -DBT	6.6	7.3	8.8	10.2	9.3
4-6 DMDBT	26.4	28.8	33.1	40.5	35.1
3-6 DMDBT	22.6	27.1	32.3	37.0	34.0
2-4 DMDBT	36.8	44.4	53.4	68.7	66.0
2-8 DMDBT	21.9	24.4	25.9	28.8	26.9
1-4 DMDBT	35.8	40.8	61.3	67.0	62.4
1-3 DMDBT	19.0	24.0	27.7	34.3	34.0
4-ETH -6-MDBT	11.9	12.8	14.1	17.4	13.6
2-PRO-DBT	26.4	31.4	36.4	45.7	52.0
2-4-8 TMDBT	11.8	13.8	18.9	20.3	21.2

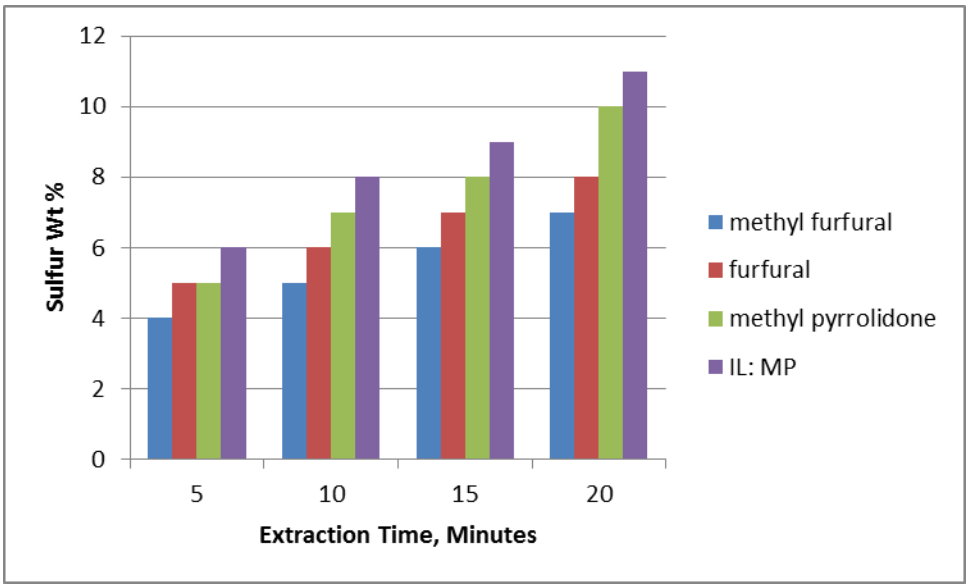


Figure 31: Total sulfur (%) extracted with various organic solvent and IL.

Methyl pyrrolidone (MP) with IL [EMIM][F3CSO3] (1:10 ratio)

5.4.2 Selecting the optimum flow rate

In this study, the optimum flow rate was investigated based on the total sulfur extraction. The experiments were conducted using various flow rates 10, 20 and 35 rpm. The porous membrane assisted flow reactor (n-methyl pyrrolidone combined with [EMIM][CF_3SO_3] for 20 minutes has been used for removal of sulfur compounds. The results showed that the total sulfur removal was increased gradually 35 followed by 20 and then 10 rpm. The percentage removal of sulfur compounds gradually increases from 10 to 13 and then 21 % during reducing the feed flow from 35 to 20 and then to 10 rpm, respectively. Accordingly, the feed flow 10 rpm was selected as the optimum flow for porous membrane assisted flow reactor. Table 36 showed that the concentration of extracted sulfur compounds increases gradually with reducing feed flow. It can noticed that the lowest feed flow 10 rpm permit the extractive solvent to interact with sulfur compounds more and accordingly extract more sulfur compounds than 20 and 30 rpm. Figure 32 illustrated the total sulfur area of extracted sulfur compounds at different feed flow 10, 20 and 30 rpm.

Table 36: Optimum feed flow for the removal of sulfur compounds using porous membrane assisted flow reactor.

Sulfur compounds	Extracted sulfur compounds conc. mg/L at flow rate 10 rpm	Extracted sulfur compounds conc. mg/L at flow rate 20 rpm	Extracted sulfur compounds conc. mg/L at flow rate 30 rpm
2-6 DMBT	7.0	5.1	3.7
2-4-DMBT	29.0	27.4	16.8
2-3-DMBT	107.9	95.3	73.0
2-3-6 TMBT	180.7	55.8	32.8
2-3-4TMBT	73.3	25.1	11.2
DBT	111.9	83.5	73.6
4-MDBT	201.7	102.5	127.5
2-MDBT+3MDBT	186.7	145.5	124.5
1-MDBT	118.0	65.0	52.4
4-ETH -DBT	20.5	14.3	10.2
4-6 DMDBT	41.5	60.5	40.5
3-6 DMDBT	138.5	72.8	37.0
2-4 DMDBT	90.2	70.1	68.7
2-8 DMDBT	53.2	39.6	28.8
1-4 DMDBT	178.8	103.3	67.0
1-3 DMDBT	67.2	36.5	34.3
4-ETH -6-MDBT	35.8	22.8	17.4
2-PRO-DBT	112.0	46.4	45.7
2-4-8 TMDBT	35.3	25.1	20.3

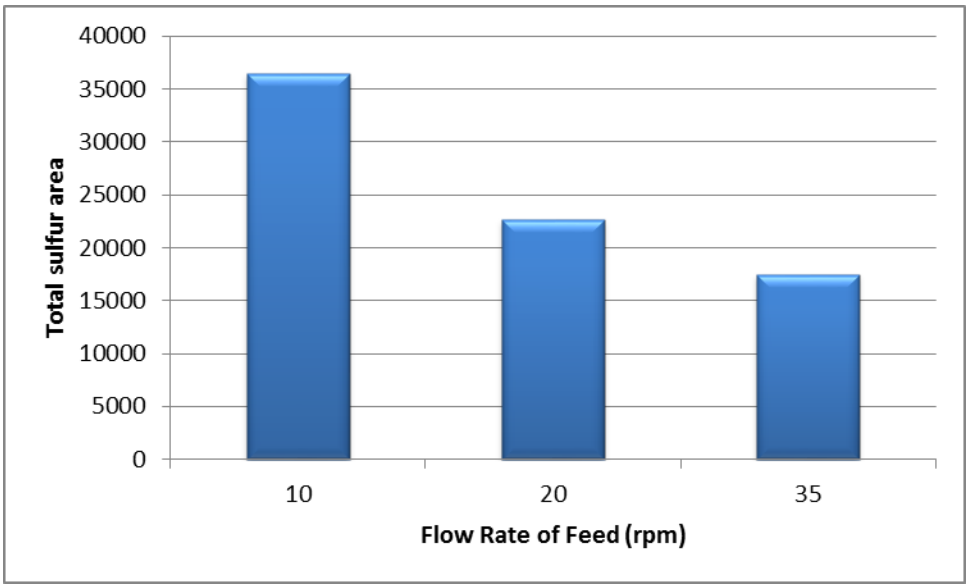


Figure 32: Total sulfur (extracted) area versus feed flow rate (rpm)

Conclusion

Removal of sulfur compounds from crude oils and fractions can be achieved using porous membrane assisted flow reactor. Various ionic liquids including ([EMIM][CF_3SO_3] and [BMPY][CH_3SO_4]) and organic solvents such as (furfural, methyl furfural and n-methyl pyrrolidone) were tested. The selected porous membrane contactor provides a contact interface between the feed and extractive solvents to allow the extractive solvents to draw sulfur compounds. The membrane has been selected based on the extractive solvent. The results indicated that the organic solvent n-methyl pyrrolidone was much better than other organic solvents for removal of sulfur compounds from crude oils and fractions. In addition, the removal of sulfur compounds were significantly increased by combining IL[EMIM][CF_3SO_3]with organic solvent n-methyl pyrrolidone using 1:10 ratio and adjust the flow rate at 10 rpm. The results showed that the concentration of sulfur compounds in the feed reduced with increasing time extraction until reaching optimum time 20-30 minutes. The results revealed that 21 % of sulfur compounds were removed from real diesel using optimum conditions e.g. (flow rate 10 rpm, extraction time 20 minutes and combination of organic solvent with IL).

CHAPTER 6

6.0 Removal of sulfur and mercury using electro-membrane

In this section, the electro-membrane assisted flow reactor technique was further optimized using various voltages to enhance the percentage removal of sulfur compounds. Negative electrode was immersed into the donor phase whereas positive electrode was immersed into acceptor phase. The aim of applying voltage is to expedite and force the sulfur ions migrations to the acceptor phase as well as enhance the interaction between acceptor and donor phases. This method was further optimized based on the highest percentage removal of sulfur compounds.

6.1 Material and chemical

The solvents (IL combined with organic solvents) and membrane were described in chapter 3. The close flow reactor cell was described in chapter 5. A slight modification was added in the reactor cell by introducing metal wire to the solvent and sample compartment, as shown in Figure 33.

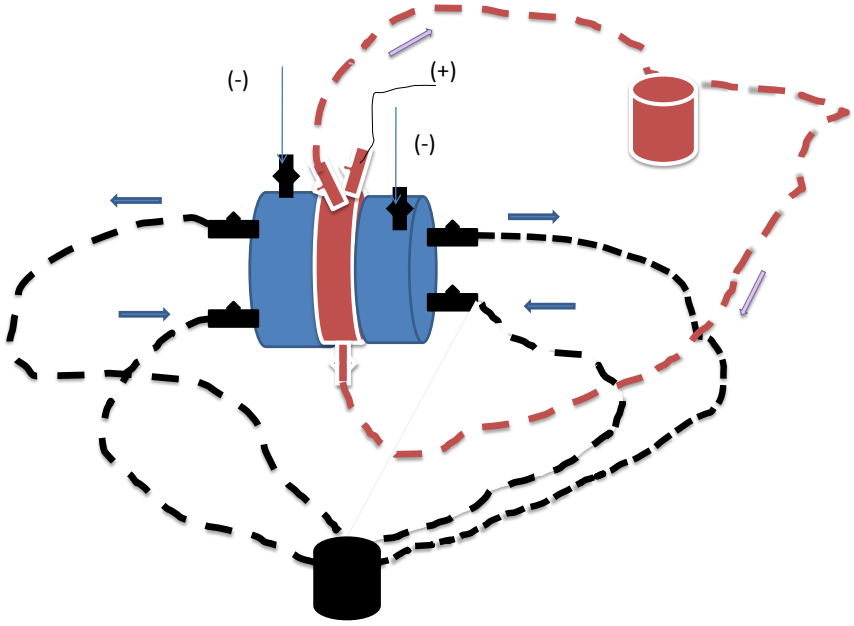


Figure 33: Electro-membrane assisted flow reactor

6.2 Experiments

The experiment of porous membrane assisted flow reactor combined with voltage was conducted in two steps:

1- Organic solvent (n-methyl pyrrilidone) was used as extractive solvent

7 ml of methyl pyrrilidone was added into the solvent compartment and 100 ml of diesel sample was added into sample container. The removal of sulfur compounds was investigated at various voltages (10, 50, 100 and 200 V). Flow rate and extraction time were identified in the previous chapter (20 minutes and 10 rpm).

2- Combination of organic solvent with ionic liquid supported with voltage

The organic solvent (n-methyl pyrrolidone) was combined with ionic liquid [EMIM][CF_3SO_3] in a ratio 1:10, IL: organic solvent. 7 ml of this ratio was taken and added into the solvent compartment and 100 ml of feed was studied. The experiment was conducted at various voltages e.g. 10, 50, 100, 200 V. In addition, the optimum conditions flow rate and extraction time were 10 rpm and 20 minutes.

6.3 Result and discussion

6.3.1 Extraction optimum time

The study was conducted at various times (5,10,15, 20 and 30 minutes) to identify the optimum extraction time. The results showed that the removal of sulfur compounds increases with increasing extraction time until reach the optimum time 20-30 minutes, as shown in Table 37. The results revealed that the percentage removal of sulfur compounds increases along with increasing extraction time from 5 to 30 minutes from 10 - 28 %, respectively. In addition, the results showed that the percentage removal of sulfur compounds increases with increasing voltage, as shown in Table 38. The optimum voltage was 100 V. However, the percentage removal of sulfur compounds increases from 30 % to 44 % due to enhancing the extractive solvents efficiency by combining IL [EMIM][CF_3SO_3] with organic solvent (n-methyl pyrrolidone) and used the optimum experiment conditions e.g. voltage 100 V, flow rate 10 rpm, recycling time 20 minutes and 1:10 ratio IL: organic solvent. Table 37 shows the concentration of extracted sulfur compounds, at various extracting times, using this method at voltage 50 V and flow rate 10 rpm. N-methyl pyrrolidone was used alone in this experiment.

Table 37: Concentration of extracted sulfur compounds using electro-membrane assisted flow reactor at various extraction times.

Sulfur compounds	5 minutes mg/L	10 minutes mg/L	15 minutes mg/L.	20 minutes. mg/L	30 minutes. mg/L
2-6 DMBT	3.2	5.6	7.5	8.7	8.0
2-4-DMBT	26.7	45.4	67.6	78.3	73.7
2-3-DMBT	69.2	117.1	148.5	215.9	206.2
2-3-6 TMBT	72.6	139.5	188.2	259.5	248.9
2-3-4TMBT	27.8	55.8	96.4	111.8	101.1
DBT	62.9	102.6	131.1	196.0	177.8
4-MDBT	63.3	103.3	155.0	195.8	170.8
2-MDBT+3MDBT	78.5	133.1	195.3	231.7	215.4
1-MDBT	34.3	54.7	67.2	93.6	89.6
4-6 DMDBT	43.1	81.8	131.8	150.6	140.8
3-6 DMDBT	53.3	97.3	119.5	181.0	173.9
2-4 DMDBT	32.8	52.9	88.2	100.3	73.6
2-8 DMDBT	30.7	50.7	70.0	93.7	83.0
1-4 DMDBT	63.2	134.1	208.8	242.8	212.7
1-3 DMDBT	12.8	22.2	34.0	49.2	44.4
4-ETH -6-MDBT	18.9	45.9	74.4	85.5	82.8
2-PRO-DBT	22.8	32.1	40.7	48.5	42.8

Table 38 illustrates the extracted sulfur compounds from diesel using porous membrane assisted flow reactor at various voltages, 20 minutes extraction time and 10 rpm flow rate. N-methyl pyrrolidone was used alone in this experiment. The results showed that the percentage removal of sulfur compounds gradually increases with increasing the voltage 10, 50, 100 and 200 V to 16, 30 and 34 % and then began to stabilize after 100 V.

As can be noticed that the concentration of sulfur compounds removal increases at high voltage as well as the percentage of sulfur compounds removal was increased to 44% using optimum parameters e.g. flow rate 10 rpm, combining IL: organic solvent, voltage 100 v, as shown in Table 38 and Figure 34.

Table 38: Concentration of extracted sulfur compounds at various voltages

Sulfur compounds	Sulfur comp. mg/L at10 voltage	Sulfur comp. mg/L at50 voltage	Sulfur comp. mg/L at100 voltage	Sulfur comp. mg/L at200 voltage
2-6 DMBT	4.9	8.7	9.4	9.0
2-4-DMBT	50.3	78.3	85.8	82.1
2-3-DMBT	145.4	215.9	233.7	220.4
2-3-6 TMBT	105.8	259.5	270.6	280.7
2-3-4TMBT	46.1	111.8	125.2	112.0
DBT	89.4	196.0	207.7	192.5
4-MDBT	80.0	195.8	248.3	224.2
2-MDBT+3MDBT	82.3	231.7	266.2	248.0
1-MDBT	62.6	93.6	121.9	106.1
4-ETH -DBT	20.0	29.1	33.4	29.4
4-6 DMDBT	75.3	150.6	164.7	164.7
3-6 DMDBT	69.0	181.0	198.9	184.2
2-4 DMDBT	67.5	100.3	115.4	94.8
2-8 DMDBT	64.6	93.7	109.6	112.7
1-4 DMDBT	154.9	242.8	281.6	247.4
1-3 DMDBT	21.9	49.2	52.3	39.8
4-ETH -6-MDBT	49.1	85.5	85.5	82.0
2-PRO-DBT	15.0	48.5	50.7	49.3
2-4-8 TMDBT	21.5	31.7	29.7	29.2

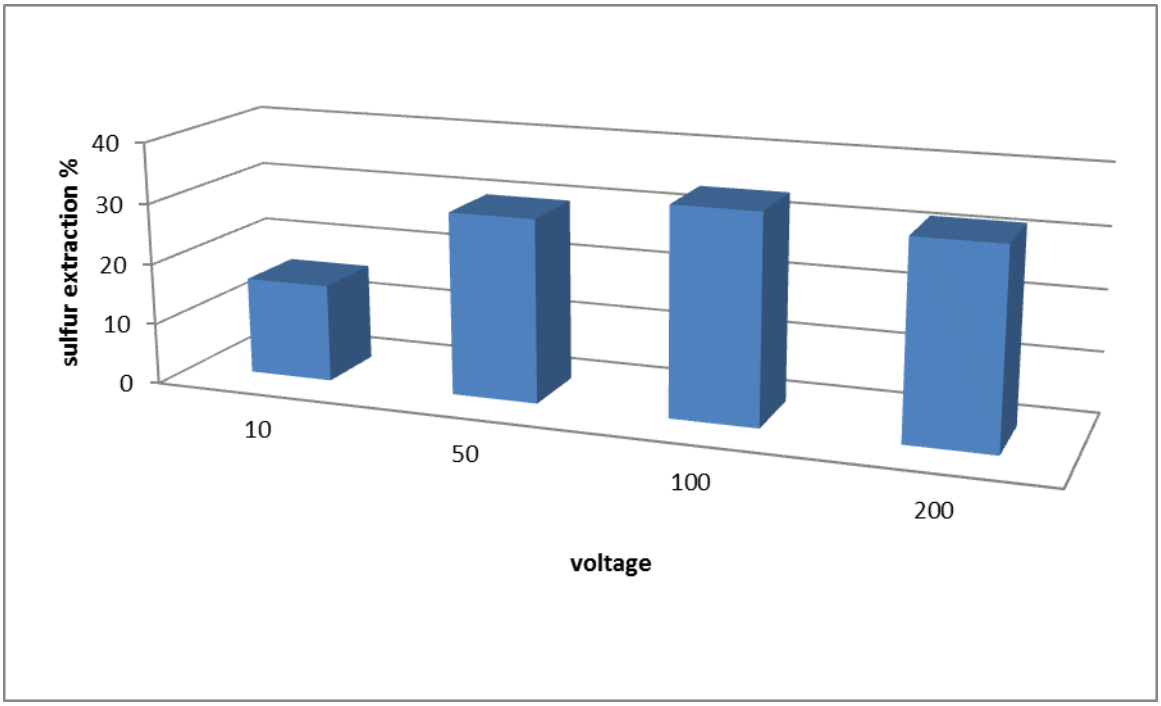


Figure 34: Total sulfur extraction (%) on applied voltages

Table 39: Removal of sulfur compounds using combination of IL with organic solvent as well as voltage 100 and flow rate 10 rpm.

Sulfur compounds	100 voltage
2-6 DMBT	8.7
2-4-DMBT	78.3
2-3-DMBT	215.9
2-3-6 TMBT	259.5
2-3-4TMBT	111.8
DBT	196.0
4-MDBT	195.8
2-MDBT+3MDBT	231.7
1-MDBT	93.6
4-ETH -DBT	29.1
4-6 DMDBT	150.6
3-6 DMDBT	181.0
2-4 DMDBT	100.3
2-8 DMDBT	93.7
1-4 DMDBT	242.8
1-3 DMDBT	49.2
4-ETH -6-MDBT	85.5
2-PRO-DBT	48.5
2-4-8 TMDBT	31.7

6.4 Applications of electro-membrane flow reactor

This method porous membrane assisted flow reactor was further investigated for removal of sulfur , nitrogen and mercury compounds from heavy, medium and light crude oils as well as from fractions. The optimum conditions e.g. apply the appropriate voltage 100 v, extraction time 20 minutes , sample volume 100 ml and ratio between organic solvent (n-methyl pyrrolidone) and IL [EMIM][CF_3SO_3] 1:10 have been used.

The investigation was conducted in the following order:

6.4.1 Removal of sulfur compounds from diesel

In this study, the sulfur compounds in diesel were measured before and after electro-membrane assisted flow reactor.

The results revealed that:

1- The total area of sulfur compounds in diesel reduced up to 44% of sulfur compounds from diesel, as shown in Table 40.
2- The concentration of benzothiophen compounds reduced after extraction process in the range of 50-60%, but benzothiophene compounds reduced in in the range of 10 to 62.6 %. It can be noticed that this technique was able to reduce dibenzothiophene up to 63 %.

Table 40: Results of removal of sulfur compounds from diesel using electro-porous membrane assisted flow reactor:

Sulfur compounds	Conc. before treatment mg/L	Conc. after treatment mg/l	Recovery %
2-6 DMBT	40	16.0	60.0
2-4-DMBT	280	127.0	54.6
2-3-DMBT	630	403.0	36.0
2-3-6 TMBT	890	431.0	51.6
2-3-4TMBT	402	194.0	51.7
DBT	620	232.0	62.6
4-MDBT	770	353.0	54.2
2-MDBT+3MDBT	600	407.0	32.2
1-MDBT	320	213.0	33.4
4-ETH -DBT	160	82.0	48.8
4-6 DMDBT	460	321.0	30.2
3-6 DMDBT	810	299.0	63.1
2-4 DMDBT	200	164.0	18.0
2-8 DMDBT	280	222.0	20.7
1-4 DMDBT	670	412. 0	38.5
1-3 DMDBT	140	86.0	38.6
4-ETH -6-MDBT	240	131.0	45.4
2-PRO-DBT	120	107.0	10.8
2-4-8 TMDBT	190	171.0	10.0

6.4.2 Removal of sulfur compounds from Arabian light crude oil using electro-membrane approach

Arabian light crude oil was extracted using electromembrane approach. Concentrations of sulfur compounds were determined before and after the extraction using GC-SCD.

The results showed that:

1- Total area of sulfur compounds in light crude oil reduced up to 57 % (Table 41 and Figure 35).
2- The concentration of benzothiophen compounds reduced in the range of 50-66%, but benzothiophene compounds reduced ranging bewteen 40 to 78 %. It can be noticed that 78 % of DBT was also reduced using this method.

Table 41: Removal of sulfur compounds from Arabian light crude oil using electro-membrane flow reactor:

Sulfur compounds	Conc. Before treatment mg/L	Conc. after treatment mg/L	Recovery %
2-6 DMBT	15	7	53
2-4-DMBT	60	24.0	60
2-3-DMBT	70	33.0	53
2-3-6 TMBT	12	6.0	50
2-3-4TMBT	140	47.0	66
DBT	107	24.0	78
4-MDBT	260	75.0	71
2-MDBT+3MDBT	210	59.0	72
1-MDBT	180	70.0	61
4-ETH -DBT	90	42.0	53
4-6 DMDBT	180	87.0	52
3-6 DMDBT	310	138.00	55
2-4 DMDBT	172	87.0	49
2-8 DMDBT	210	110.0	47
1-4 DMDBT	280	154.0	45
1-3 DMDBT	75	38.0	49
4-ETH -6-MDBT	180	88.0	51
2-PRO-DBT	80	19.0	76
2-4-8 TMDBT	45	26.0	42

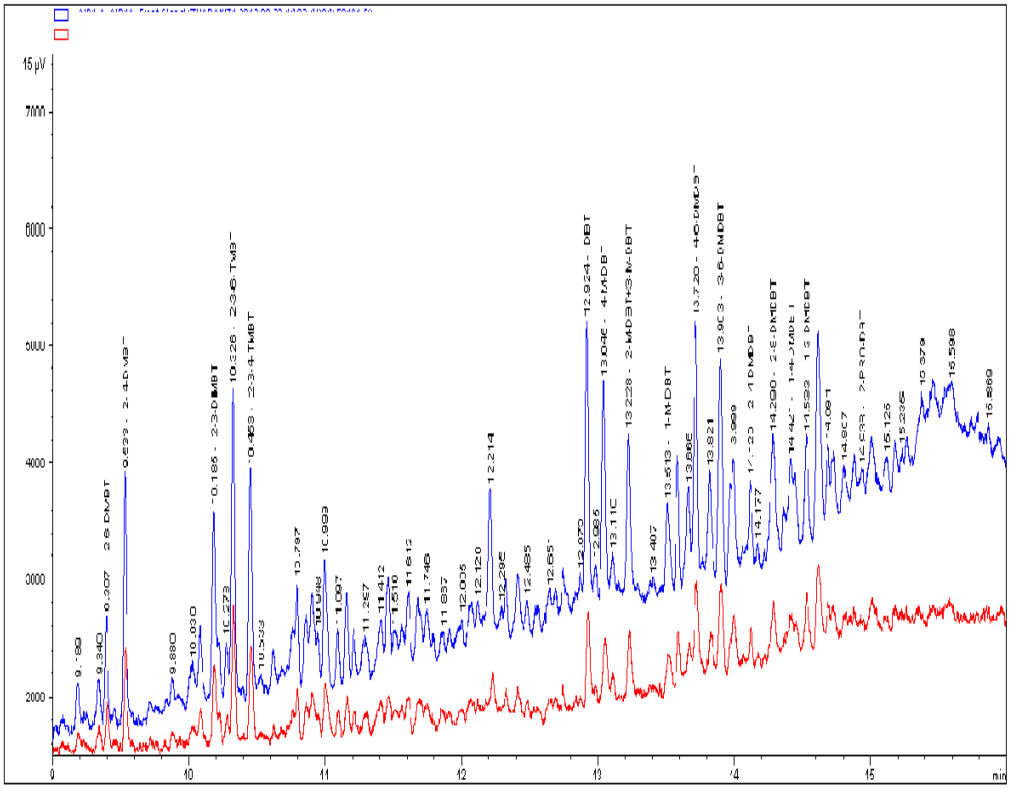


Figure 35: GC-SCD chromatogram of sulfur target analytes of AL crude oil and product. Feed (in blue) and product, after porous membrane assisted flow reactor (in red)

6.4.3 Removal of sulfur compounds from Arabian medium crude oil suing electro-membrane

Arabian medium crude oil samples were extracted and analyzed by GC-SCD to determine the sulfur compounds. The results showed that:

1- 52 % of target sulfur compounds was reduced form AM crude oil, (Table 42 and Figure 36).
2- The percentage recovery of BTs was in the rage of 35 to 60 %. However, DBTs was in the range of 34 – 61%.

Table 42: Removal of sulfur compounds from Arabian medium crude oil using electro membrane flow reactor.

Sulfur compounds	Conc. before treatment mg/L	Conc. after treatment mg/L	Recovery %
2-6 DMBT	28	11.0	60.7
2-4-DMBT	84	48.0	42.9
2-3-DMBT	21	16.0	23.8
2-3-6 TMBT	205	138.	32.7
2-3-4TMBT	101	66.0	34.7
DBT	144	95.0	34.0
4-MDBT	298	137. 0	54.0
2-MDBT+3MDBT	246	175.0	28.9
1-MDBT	223	108.0	51.6
4-ETH -DBT	114	51. 0	55.3
4-6 DMDBT	242	150. 0	38.0
3-6 DMDBT	205	102. 0	50.2
2-4 DMDBT	390	154.0	60.5
2-8 DMDBT	233	97. 0	58.4
1-4 DMDBT	310	708.0	49.7
1-3 DMDBT	109	47.0	56.9
4-ETH -6-MDBT	210	90.0	57.1

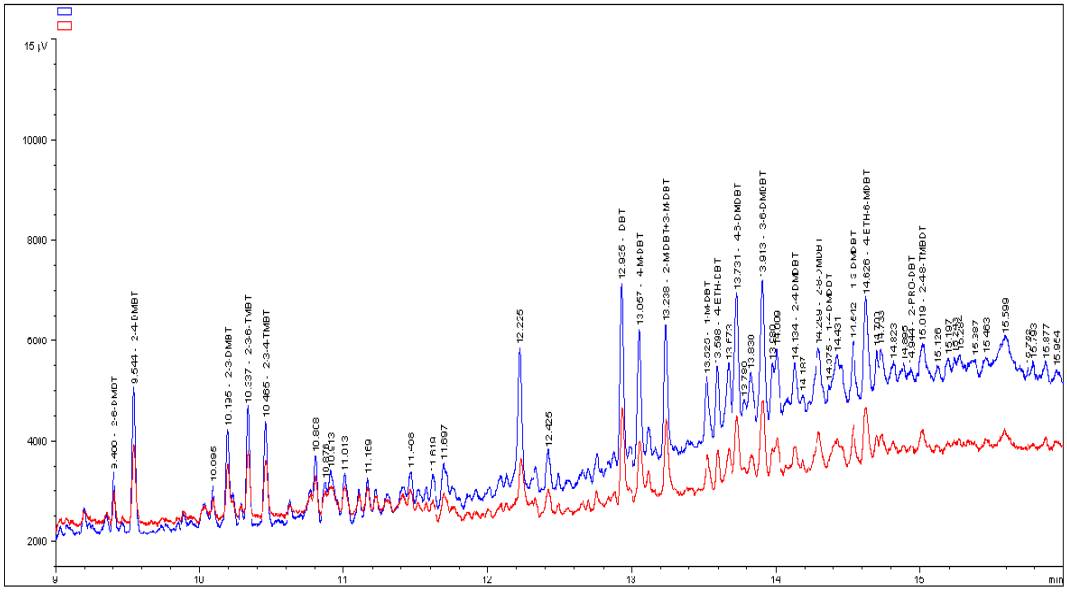


Figure 36: GC-SCD chromatogram of sulfur target analytes of AM crude oil and product. Feed (in blue) and product, after porous membrane assisted flow reactor (in red)

6.4.4 Removal of sulfur compounds from Arabian heavy crude oil suing electro-membrane

This method was also used to evaluate the removal of sulfur compounds from Arabian heavy crude oil. The results revealed that 48 % of target sulfur compounds was reduced, as shown in Table 43 and Figure 37. In addition, the percentage of BTs was reduced in the range of 47 – 60 %, but the DBTs was reduced in the range of 20- 50%.

Table 43: Results of sulfur containing compounds removal from AH crude oil using electro-membrane assisted flow reactor.

Sulfur compounds	Conc. Before treatment mg/L	Conc. after treatment mg/L	Recovery (%)
2-6 DMBT	40	16	60.0
2-4-DMBT	105	40	61.9
2-3-DMBT	38	20	47.4
2-3-6 TMBT	260	128	50.8
2-3-4TMBT	145	76	47.6
DBT	210	170	19.0
4-MDBT	315	205	34.9
2-MDBT+3MDBT	276	140	49.3
1-MDBT	280	250	10.7
4-ETH -DBT	164	64	61.0
4-6 DMDBT	280	110	60.7
3-6 DMDBT	245	107	56.3
2-4 DMDBT	496	355	28.4
2-8 DMDBT	276	135	51.1
1-4 DMDBT	384	192	50.0
1-3 DMDBT	135	68	49.6
4-ETH -6-MDBT	260	131	49.6
2-4-8 TMDBT	140	82	41.4

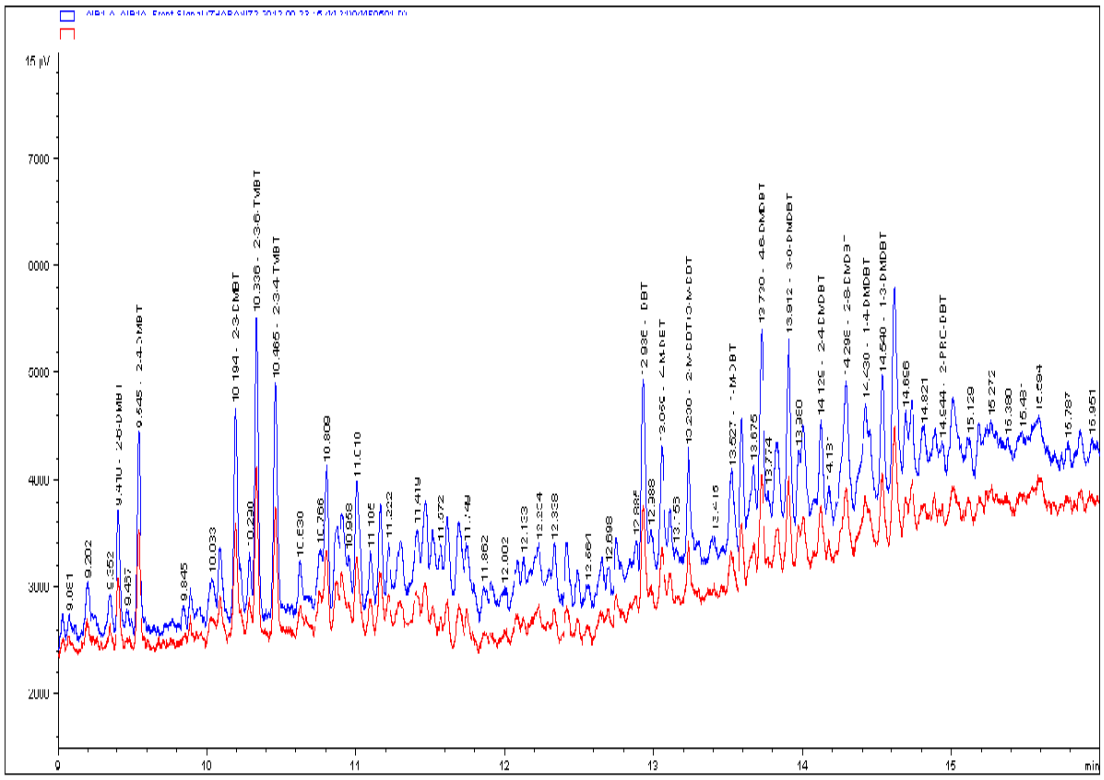


Figure 37: GC-SCD chromatogram of sulfur target analytes of AH crude oil and product. feed (in blue) and product (in red)

CHAPTER 7

7.0 Sulfur compounds measurement using X-ray Fluorescence (XRF) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS)

XRF and FT-ICR-MS were commonly used to quantitate total sulfur compounds. Thus we extend out work to determine the total sulfur using XRF and FT-ICR-MS techniques. The crude oils and fractions samples were analyzed before and after each extraction.

7.1 XRF applications and characteristics

The XRF techniques are widely used in the petrochemical field due to its sensitivity and selectivity. Fluorescence has also been used in the petroleum industry for the analysis of elemental composition of oils. XRF is fast, accurate and non-destructive method for elemental analysis and chemical analysis.

7.2 X-ray Fluorescence (XRF) principle

X-rays have a short wavelength in the range of 10 to 0.01 nanometers. Ahigh energy X-ray photons is emitted from an X-ray source (X-ray tube) and strikes the sample. The high energy X-ray photons will relocate the electrons position from (K or L) orbitals, resulting atoms become ions. However, these ions are not stable. Consequently, they will move to more stable orbital from an outer into a vacant stable inner orbitals. Secondary X-ray photons will be emitted during this process of an electron moving from an outer to an inner orbital. The X-ray emission of the secondary electron depends on the target metals concentration which will be detected by X-ray detector.

7.3 Results and discussion

The XRF has been used to ascertain the total sulfur concentration of crude oils and diesel before and after each simultaneous treatment. The results revealed that 39. 4 % of total sulfur in diesel was extracted and 54.70, 52.50, 46.0 % of light, medium and heavy crude oils were also reduced, respectively, as shown in Table 44. The XRF results confirmed that the removal of sulfur compounds using electro-porous membrane assisted flow reactor.

Table 44: Total sulfur measurement by XRF of Arabian heavy, medium and light crude oils before and after porous membrane assisted flow reactor

Crude oils classifications	Total sulfur conc. Before treatment	Total sulfur conc. After treatment	Extraction (%)
Arabian light crude oil	1.95	0.883	54.70
Arabian medium crude oil	2.80	1.33	52.50
Arabian heavy crude oil	2.97	1.60	46.0
Diesel	0.127	0.077	39.40

7.4 Sulfur compounds analysis by FT-ICR MS APPI

FT-ICR MS APPI has been used to perform a comprehensive characterization of carbon number and DBE distributions of the diesel samples (chapter 3). Figure 38 shows an exemplary plot that compiles the chemical information obtained from such a mass spectrometric analysis and can be summarized as follows:

1- The beige area marks the petroleum continuum, i.e., the elemental compositions valid for petroleum molecules.
2- The maximum number of aromatic carbon atoms per molecule is designated by the diagonal red line.
3- Red line shows purely aromatic hydrocarbons without alkyl groups, whereas aromatic molecules with alkyl chain(s) fall below the red line into the petroleum continuum.
4- The red zone in the upper right corner indicates the molecular structures associated with asphaltenes.
5- Black dots indicate aromatic compounds structures, i.e. structures that contain only sp2 hybridized “aromatic” carbon atoms and no aliphatic carbon atoms. Grey dots represent species that also include saturated (naphthenic) rings in addition to aromatic rings. White dots indicate alkylated species, i.e. species with carbon atoms in any form of alkyl side chains
6- Molecules with one or more naphthenic rings have been commonly observed in petroleum compositions, as well as benzologue molecules. These components appear as horizontal series of dots at a DBE value that is 3 higher than their base series, e.g. alkylbenzenes at DBE=4 and alkylnapthenes at DBE =7 (not shown).

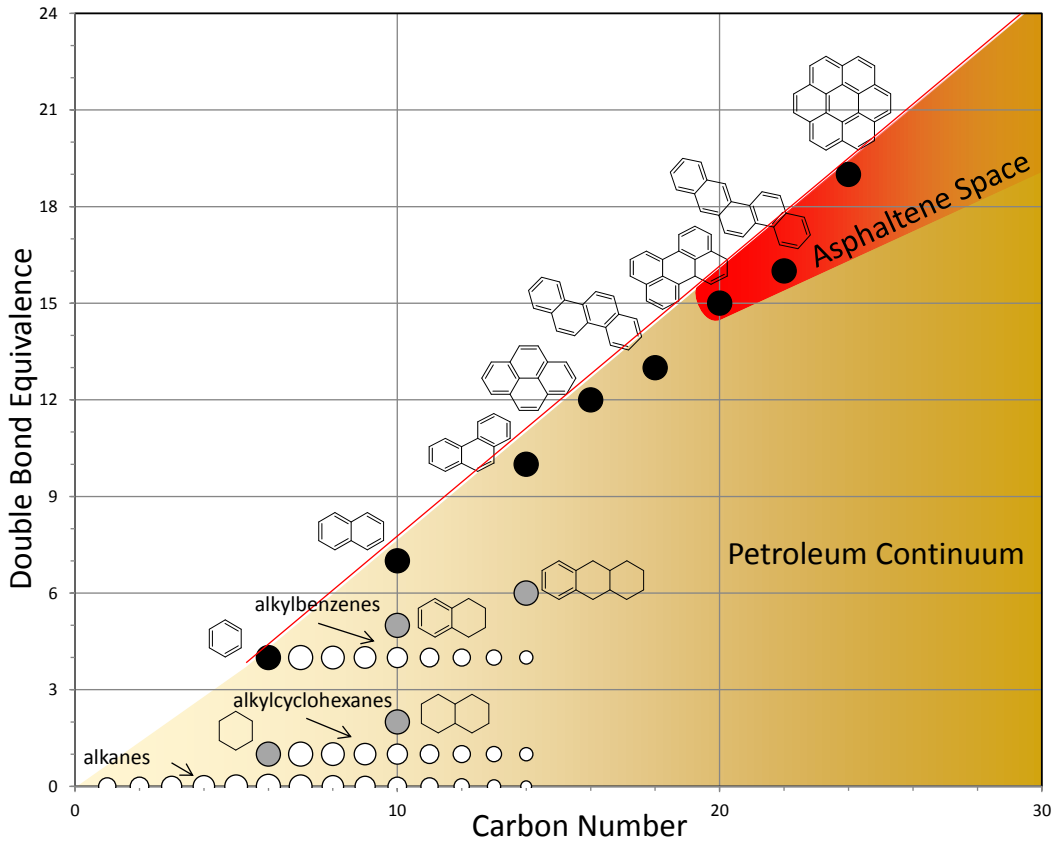


Figure 38: Schematic Carbon number vs. DBE plot illustrates diesel the chemical information obtained by mass spectrometry.

7.4.1 Diesel “Feed” composition

FT-ICR MS APPI has been used for sulfur compound speciation analysis in diesel samples before and after a membrane extraction process using LPME-HFM. It was also used to determine the number of Double Bond Equivalent (DBE) and Carbon number (C #) of the sulfur compounds present in the samples. A DBE series contains various molecules that share the same DBE number, regardless of their alkyl chain lengths. The Carbon number (C#) differentiates species within a DBE series. For example, ethylbenzene, propylebenzen, butylbenzene have DBE=4 and C#=8, 9, and 10, respectively. For instance, DBE=6 represents alkylated benzothiophenes, which were identified with 3 to 28 carbon atoms in alkyl chains. The results revealed that the feed diesel sample contains a significant number of sulfur species, with carbon numbers and DBE as shown in Figure 39. The results showed that the DBE numbers increase along with increasing unsaturated of aromatic compounds and had a range of 0-14, as follows:

1- DBE= 0 represent sulfides or mercaptanes.
2- DBE=1 characterize cyclic sulfides.
3- DBE=3 represent thiophenes.
4- DBE=6 represent alkylated benzothiophenes with 3 to 28 carbon atoms in alkyl chains.
5- DBE = 7 correspond to benzothiophenes with an additional naphthenic ring in their structure.
6- DBE=9 represent alkylated dibenzothiophenes with none to 22 carbon atoms in alkyl side chains.
7- DBE = 10 indicated dibenzothiophenes with an additional naphthenic ring

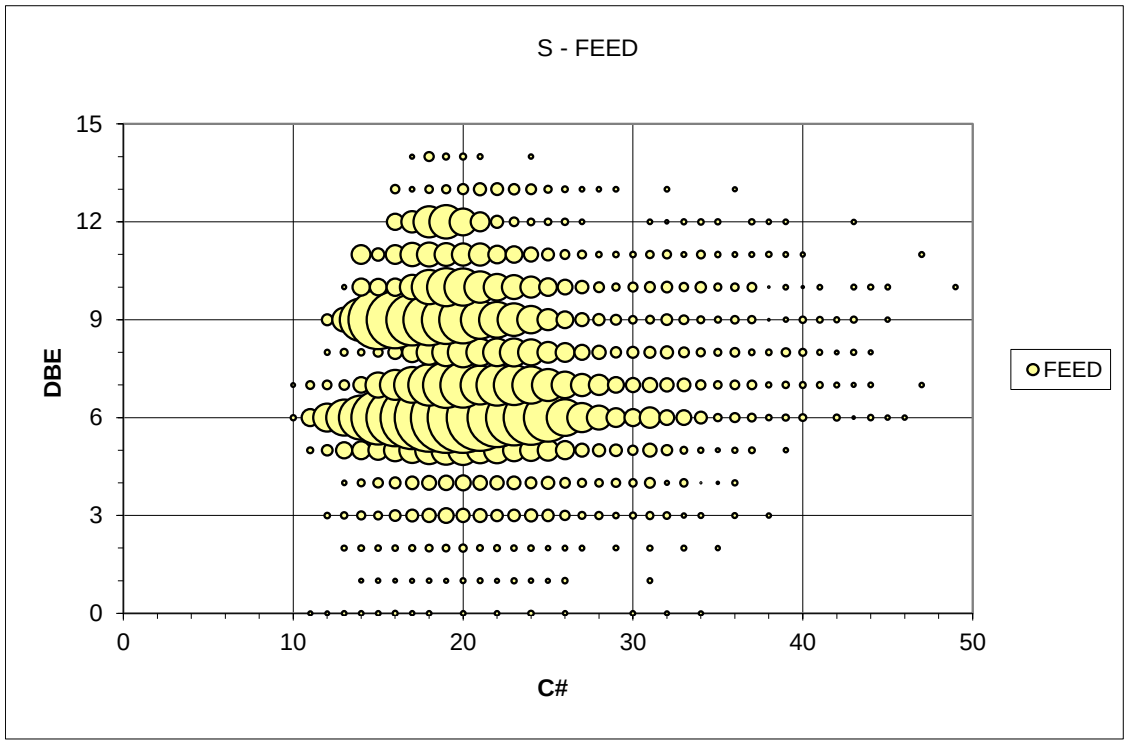


Figure 39. Carbon number vs. DBE vs. plot for sulfur species in the feed sample .

Dots at DBE=6 represent alkylbenzothiophenes and dots at DBE=9 alkyldibenzothiophenes

7.4.2 Identification of aromatic, sulfur and oxygen-sulfur compounds in diesel feed sample

In addition to sulfur containing compounds identifications, a number of other classes could be identified, namely aromatic hydrocarbons, di-sulfur, oxygen-sulfur, oxygen, and di-oxygen containing compounds. Their mass spectral abundances are listed in the graph in Figure 39 which has been obtained by summing all signal abundances of all identified mass signals for each class. It should be noted that this method cannot be used for quantification, but for comparing the composition between similar samples, e.g. the feed and the product. The results showed that the composition of diesel feed sample contains high level of hydrocarbon followed by sulfur containing compounds, oxygen-sulfur compounds, oxygenated compounds and then disulfide compounds, as illustrated in Figure 40.

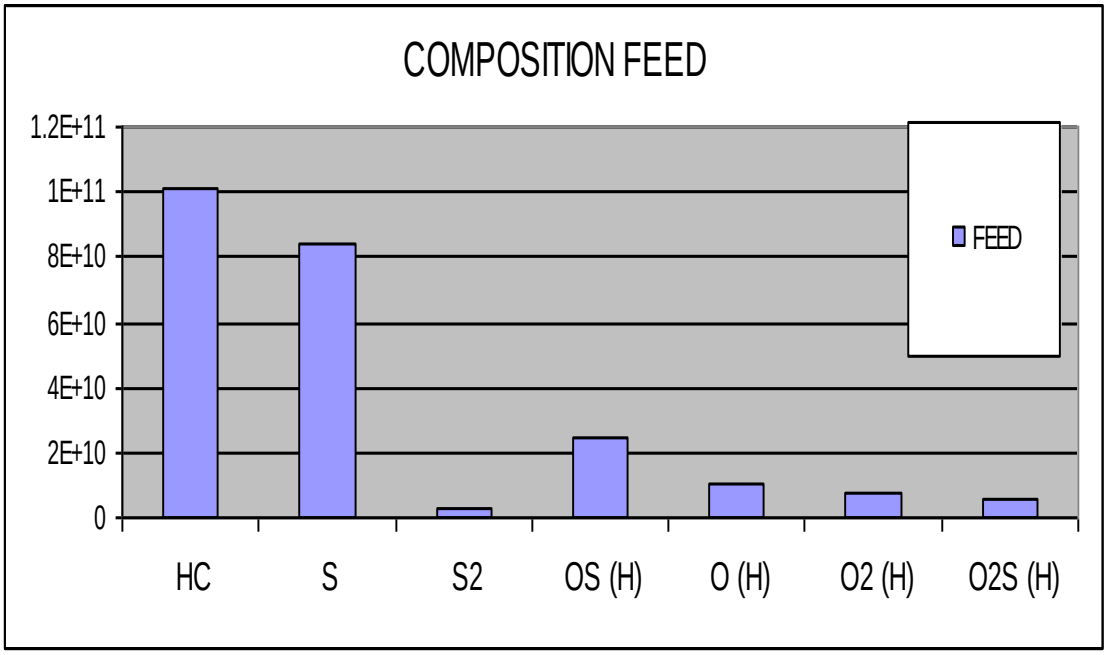


Figure 40: Summed abundances for the main heteroatom classes detected in feed diesel sample.

7.4.3 Diesel “Product” composition analysis

Figure 41 shows a comparison of the summed abundances observed for all three samples and a blank measurement. It has been observed that the sulfur containing compounds, hydrocarbons and oxygenated compounds are less abundant in the product sample and extract samples than feed sample. Blank has been used to check instrument performance. The results indicated that the sulfur containing compounds in the product as well as extractive solvent were less than in the feed diesel sample due to the membrane extraction.

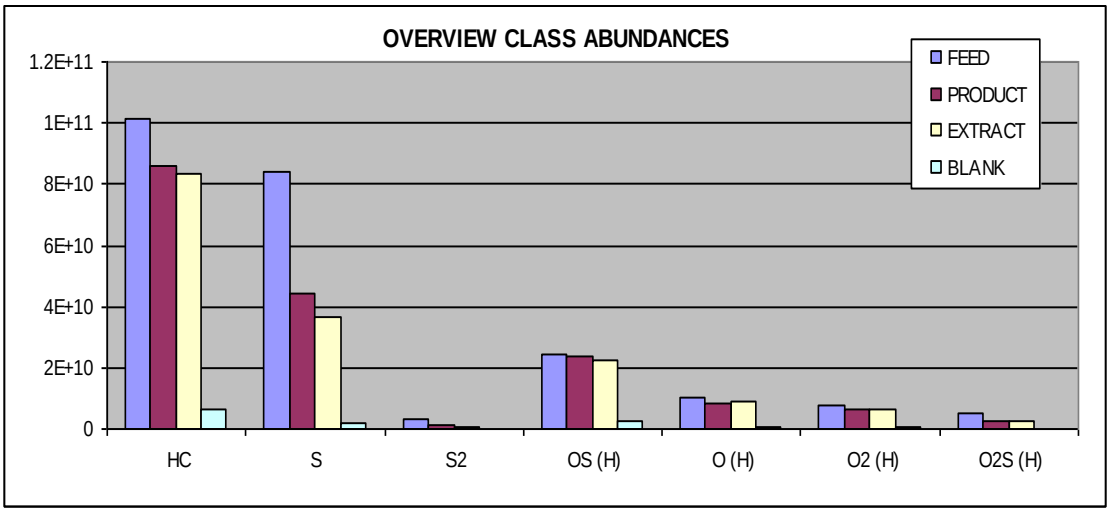


Figure 41: Summed abundances for the main heteroatom classes detected in feed, product, extract and blank sample.

7.4.4 Sulfur speciation of product diesel sample and solvent after extraction

The Figure 42 shows the DBE and C# distributions of the sulfur compounds in the product. In comparison with the feed, the product distributions appear similar. For a comprehensive picture of the extraction, the extracted sulfur species in the solvent after extraction were also determined.

7.4.5 Selectivity of Sulfur Compounds Extraction

To identify a potential selectivity of the extraction process, the DBE distributions in the feed, product, and extract samples are compared in Figure 43. The results showed that the sulfur distributions are almost identical in all three samples. In other words, the date indicates that the electro- porous membrane assisted has the potential to remove all sulfur containing compounds in the same way.

7.4.6 Light crude oil composition analysis by FT-ICR MS APPI

The high resolution FT-ICR MS APPI was used to identify the light crude oil mass spectra before and after porous membrane assisted. Exemplary mass spectral details for both, feed and product crude oil samples with identified elemental compositions are shown in Figure 45.

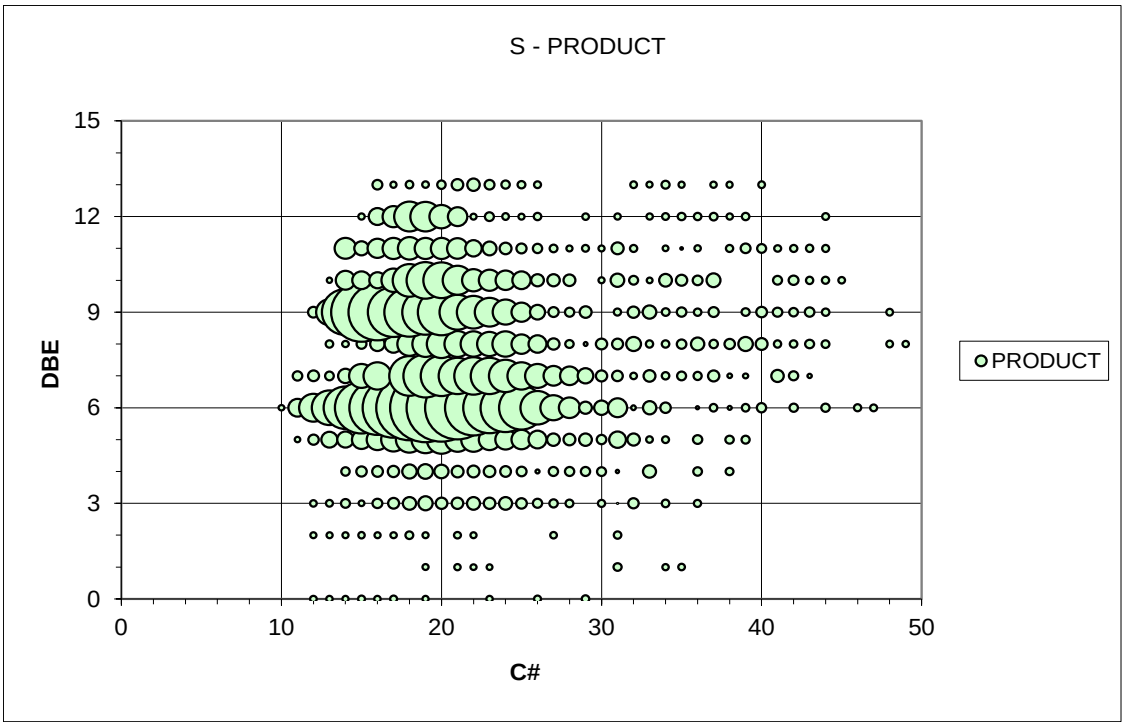


Figure 42. Carbon number vs. DBE mass spectral abundance plot of the sulfur class compounds in the product sample.

Dots at DBE=6 represent benzothiophenes and dots at DBE=9 correspond to dibenzothiophenes.

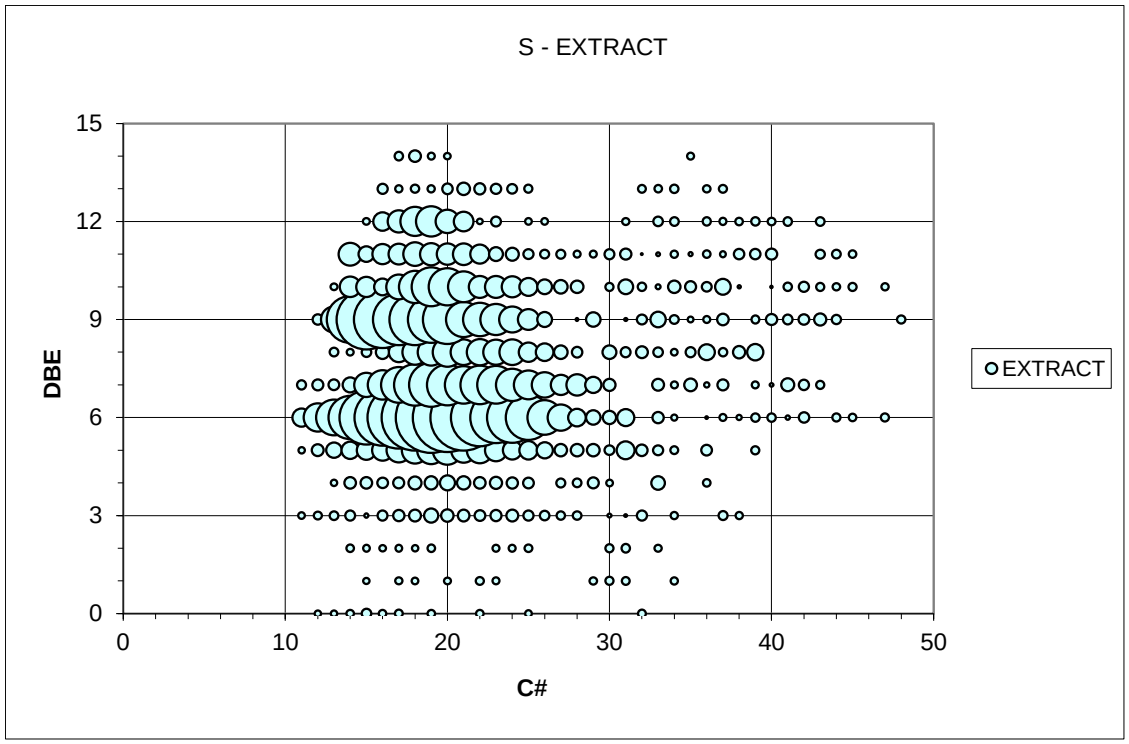


Figure 43.Carbon number vs. DBE mass spectra abundance of sulfur compounds identified in the product sample.

Dots at DBE=6 represent benzothiophenes and dots at DBE=9 correspond to dibenzothiophenes.

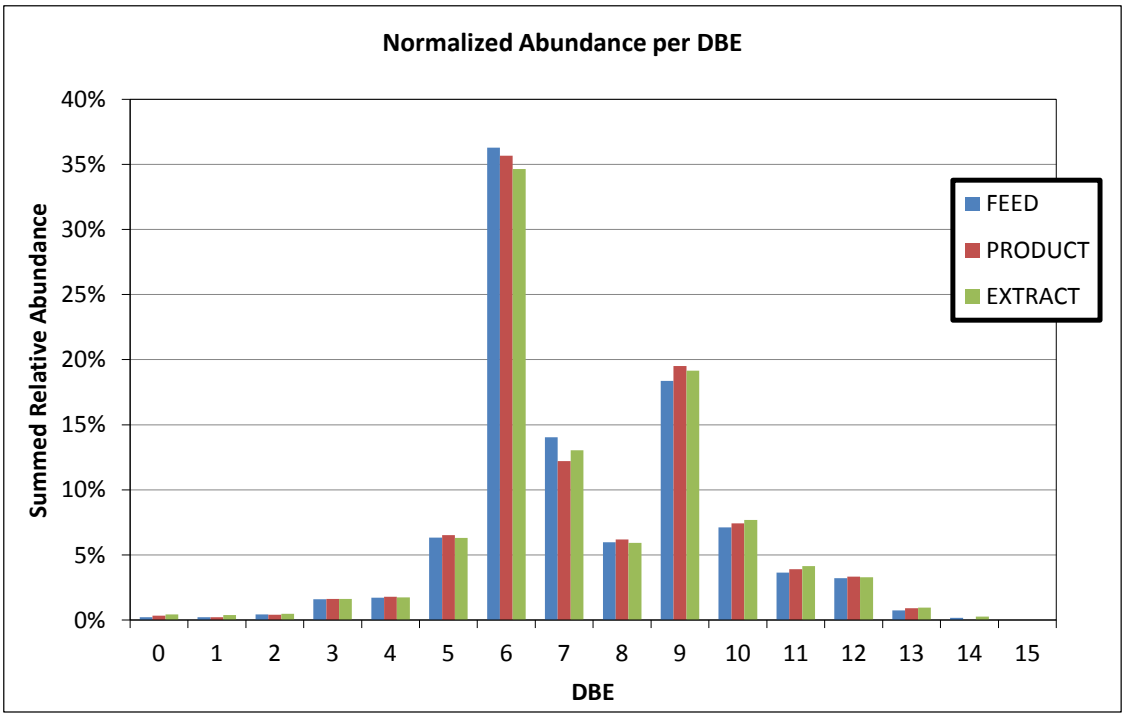


Figure 44. Normalized abundance of sulfur compounds for feed, product and extract samples.

Figure 45 shows a comprehensive visualization of the light crude oil chemical information contained in complex mass spectra in a carbon number vs. double bond equivalence vs. mass spectral abundance plot. The aromaticity of the compounds is represented by DBE. The results showed that light crude oil (feed) contains aromatic sulfur compounds with significant number of carbon atoms in alkyl chain(s), compare with product. Figure 46 shows direct comparison between samples (feed and product) can be made by looking at the relative abundances per DBE series. Comparatively, the Feed sample contains more sulfur species at DBE values from 0-6 than the Product sample. This would indicate a slight trend of sulfur compounds with DBE 6 and lower to be extracted from the Feed. The data for the Extract seems to confirm this trend as the Extract contains more low-DBE sulfur compounds.

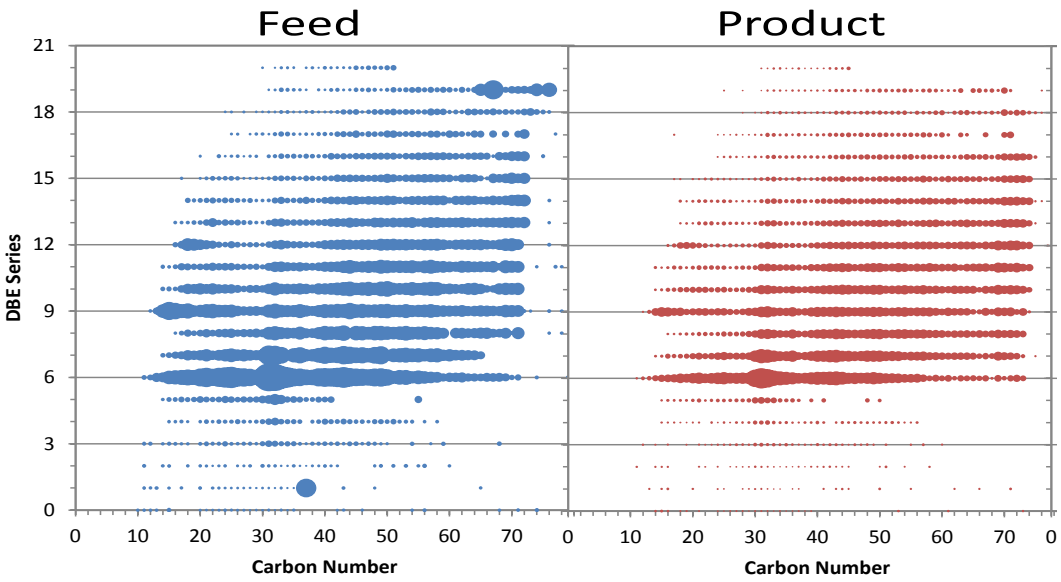


Figure 45. Carbon number vs. double bond equivalence plots of the sulfur species in Feed (left) and Product (right).

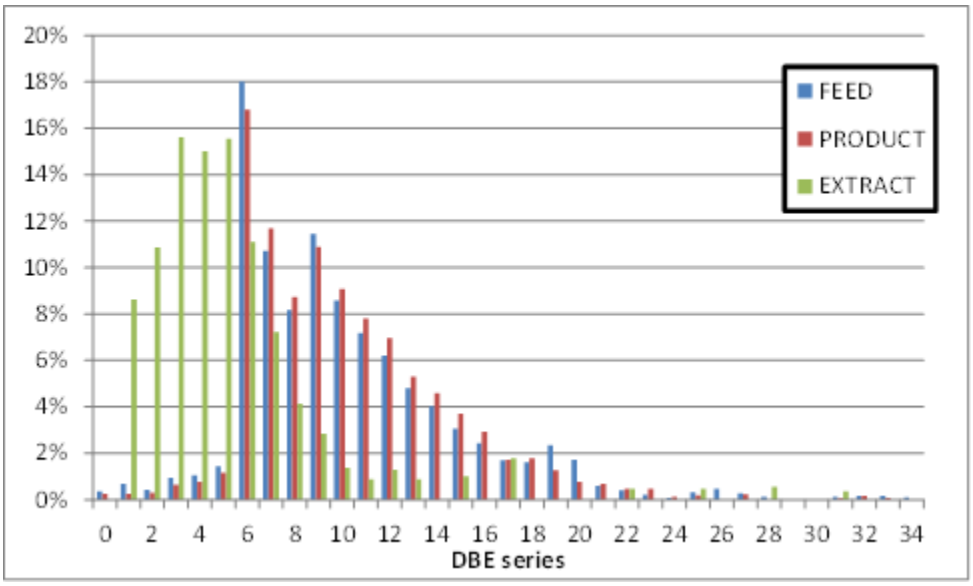


Figure 46. Relative distributions of species for feed, product and extract samples

CHAPTER 8

8.0 Removal of nitrogen compounds and mercury from crude oils and fractions using electro-membrane assisted

Application of electromembrane flow reactor was extended to investigate the removal of mercury and nitrogen compounds from crude oils (Arabian light, medium and heavy) as well as fractions. The concentration of nitrogen compounds and mercury were measured before and after porous membrane assisted flow reactor.

8.1 Mercury compounds analysis

Various mercury standards 0.5, 1 and 5 ppm were prepared from the stock mercury oil standard 100 ppm. Oil (free mercury) was used for dilution purposes. The optimum procedure (in chapter 6) was used for mercury and nitrogen compounds extraction.

8.2 Mercury results

The results showed that the concentration of Hg was reduced from 0.5 to 0.27 ppm, 1 ppm to 0.57 ppm and from 5 to 2.60 ppm, as shown in Table 45. The results indicated that porous membrane assisted flow reactor was also effective to extract mercury compounds from oils and fractions.

Table 45: Percentage recovery of mercury compounds from oil.

Mercury concentration mg/L	Mercury concentration after extraction	Recovery %
0.5	0.27	46
1	0.57	43
5	2.60	48

8.3 Nitrogen compounds analysis

Electro-membrane assisted flow reactor was also evaluated for removal of nitrogen compounds from Arabian light, medium and heavy crude oils as well as fractions using the optimum procedure e.g. (flow rate 10 rpm, 1: 10 ratio ionic liquid mixed with organic solvent, extraction time 20 minutes, voltage 100, sample volume 100 ml and solvent volume 7 ml) . The nitrogen content before and after extraction was measured using gas chromatography equipped with nitrogen detector and antek instrument.

8.4 Nitrogen results

Figure 47 showed that the crude oils and fractions contain various of nitrogen compounds e.g. acridine, carbazole and carbazole derivatives. The results indicated that the total nitrogen content was reduced from 1470 to 820 ppm of Arabian heavy crude oil, from 669 to 340 ppm of Arabian light crude oil and from 90 to 60 ppm of crude oil fractions (diesel) using electro-membrane assisted flow reactor. About 49, 44 and 33 % of total nitrogen content was reduced from Arabian light, heavy crude oil and diesel, respectively, as shown in Table 46.

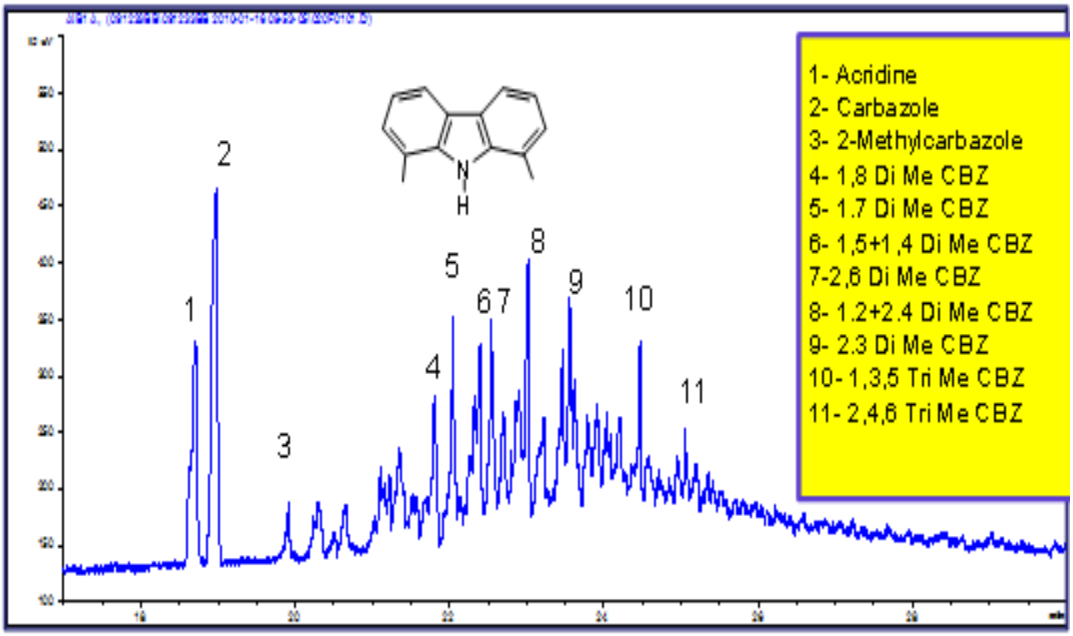


Figure 47: GC-NCD Chromatogram of nitrogen species of diesel

Table 46: Percentage recovery of nitrogen compounds from oil

Sample Type	Nitrogen content (ppm)	Nitrogen content (ppm) after extraction	Recovery (%)
Arabian light crude oil	669	340	49
Arabian heavy crude oil	1470	820	44
Diesel	90	60	33

CHAPTER 9

9.0 Characterizations of porous membrane using FTIR, TGA and ESEM

A comprehensive characterization of flat sheet and hallow fiber membrane were conducted by Thermal Gravimetric Analyzer (TGA), Fourier Transform Infrared Radiation (FTIR) and Scanning Electron Microscope (SEM). The aim of this study is to determine the membrane thermal stability, weight loss, investigate the functional groups on the membrane and identify the porous membrane thickness and porosity.

9.1 Determination of thermal stability and weight loss of the flat sheet membrane using TGA.

13 mg of the membrane sample has been loaded into the TGA sample holder. The TGA temperature was adjusted from room temperature to 900 °C under air. The results showed that the porous membrane sample starts to loss 0.1 % of its original weight at 100 °C, 1.8% at 221.88°C and > 99 % at 528.38 .The TGA results indicated that the membrane has a good thermal stability up to 200 °C and then starts to decrease as the temperature increases (Figures 48). The green curve represents the weight percent of the sample decreases as the temperature increases (°C) and the blue curve represents the rate at which the weight percent change per degree (derivative of weight percent). Around 38 % of porous membrane was lost at rate 1.3.

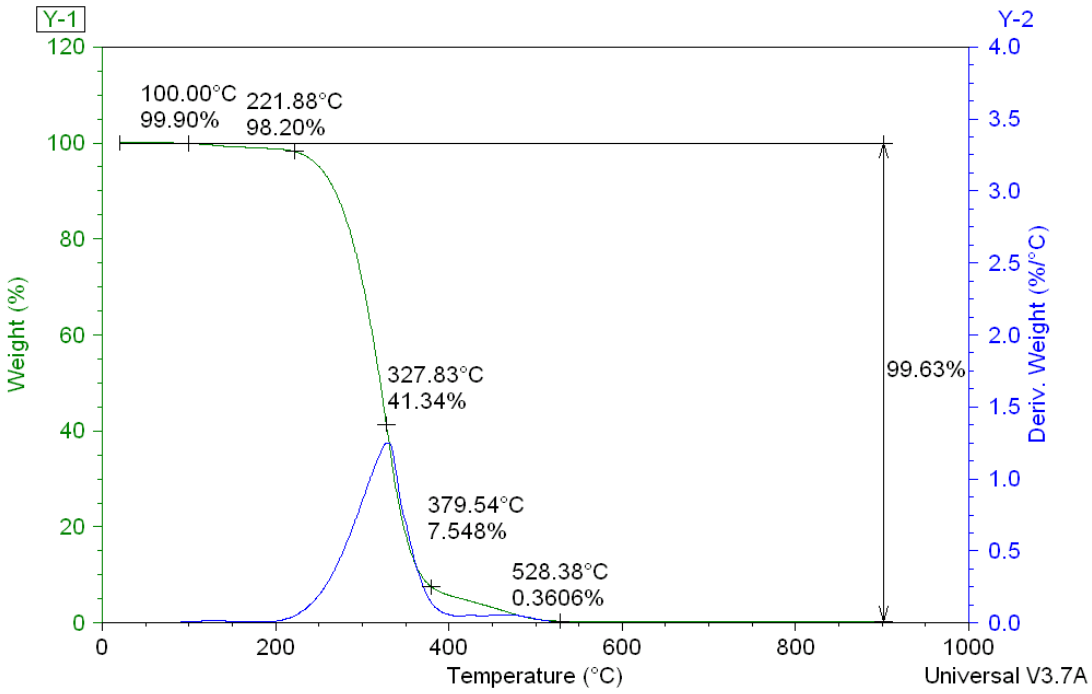


Figure 48: TGA profile of flat porous membrane sample

9.2 Identify the membrane function groups

The FT-IR with transition cell was used to identify the membrane function groups and confirm the membrane composition. Figure 49 shows that various peaks at 2950.5, 2918.3, 2868.2, 2838.3, 1457.4, 1376.4 and 1167.6 cm^{-1} were detected. The IR spectrum indicates a shoulder at 2868 and the asymmetric and symmetric in-plane C–H (–CH3) at 1457 and 1376 (shoulder) confirm the membrane composition (polypropylene) and the results revealed that the porous membrane spectrum was comparable with polypropylene spectrum.

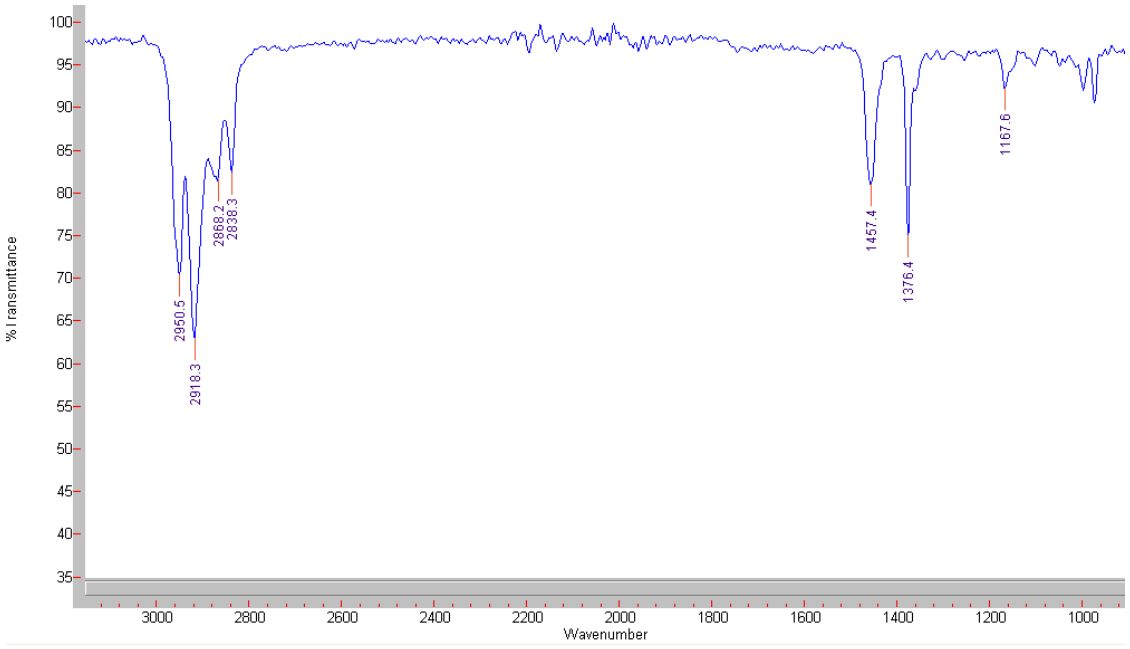


Figure 49: FTIR spectrum of the porous membrane sample

9.3 Determination of thickness and porosity of hallow fiber membrane and flat porous membrane and using scanning electron microscope (SEM)

The results indicated that the flat sheet porous membrane had porosity in the range of 0.35 to 0.70 µm and thickness 90.60 µm, as shown in Figure 50-51. Whereas, the HFM had thickness 569.54 µm, Figure 52-53.

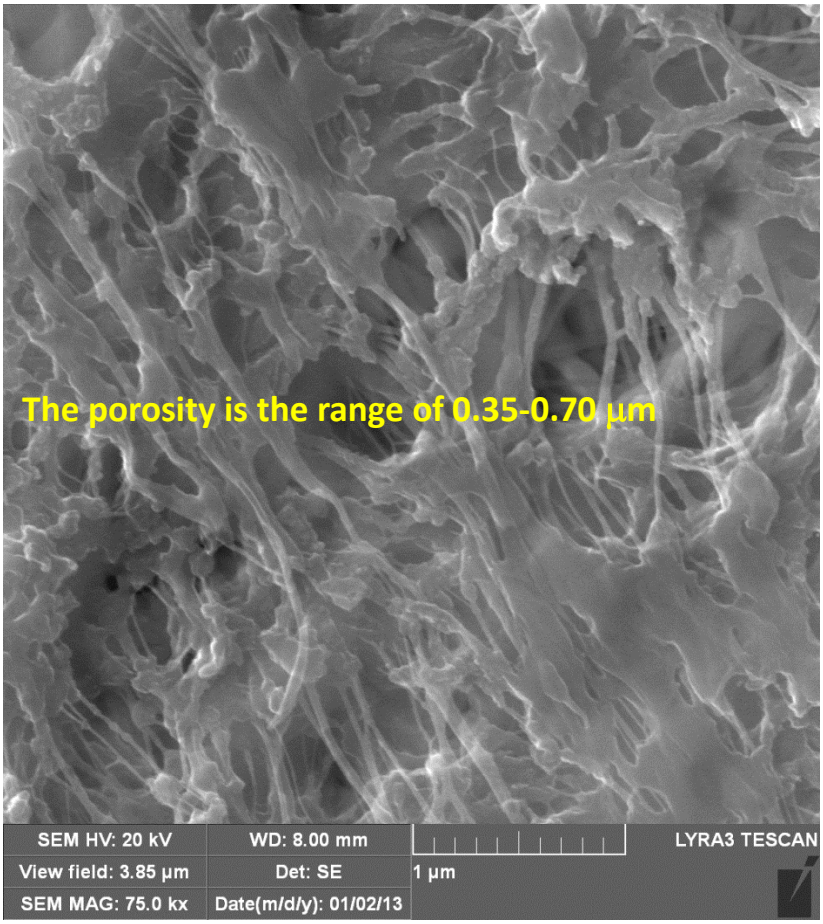


Figure 50: SEM image of flat sheet porous membrane

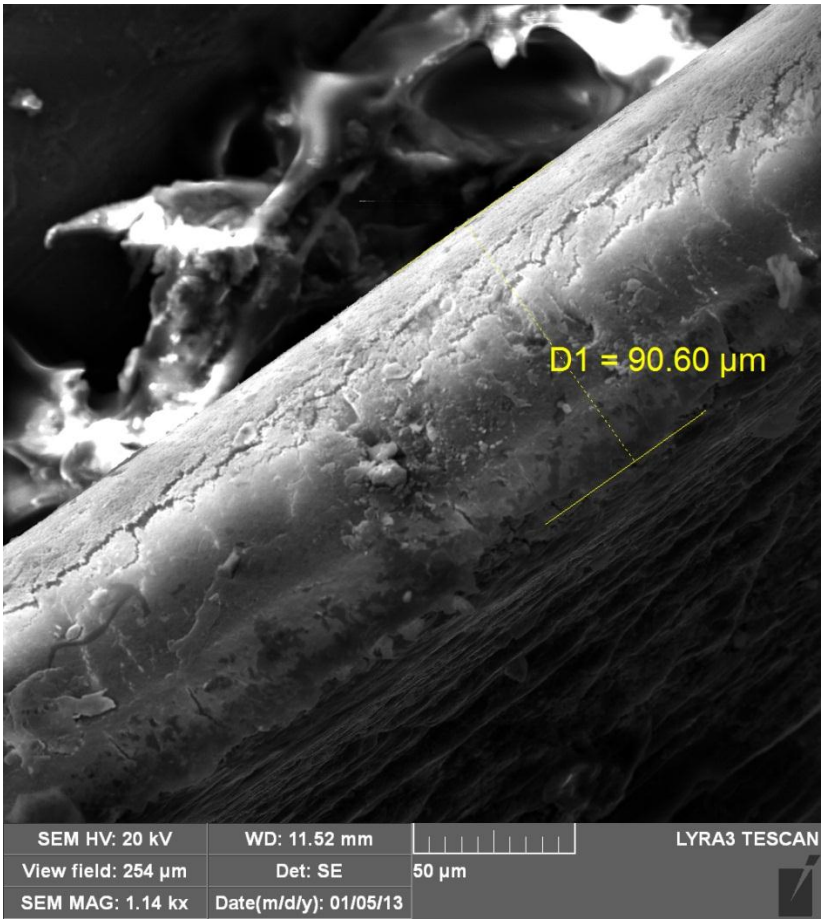


Figure 51 : SEM image of flat sheet porous membrane (thickness)

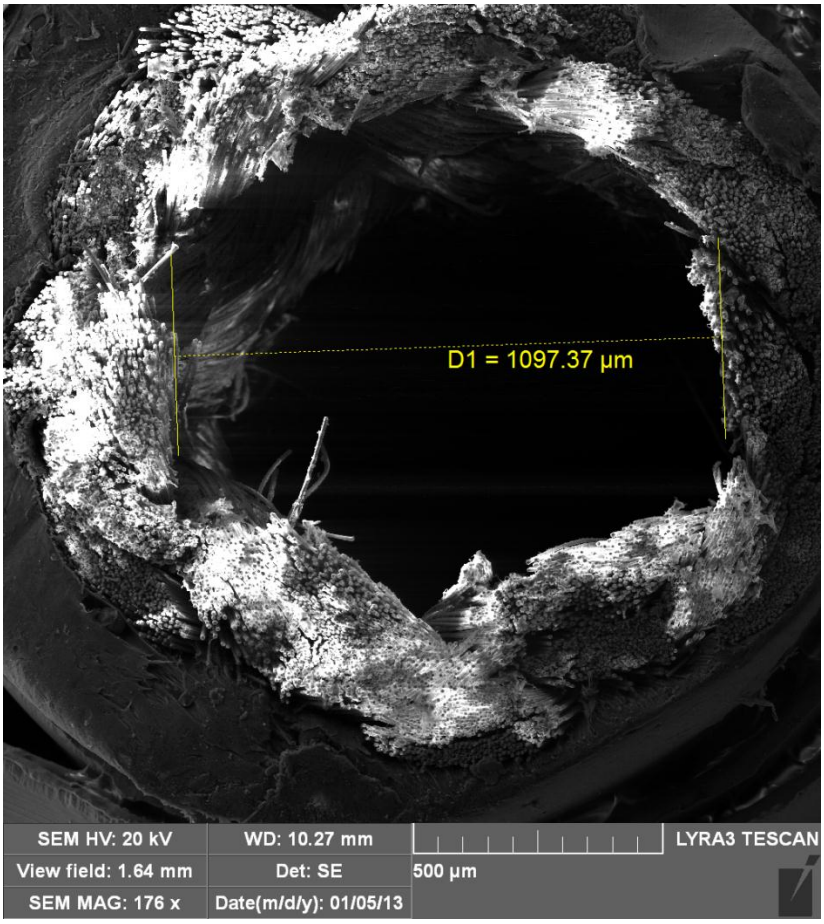


Figure 52: SEM image of HF porous membrane (thickness)

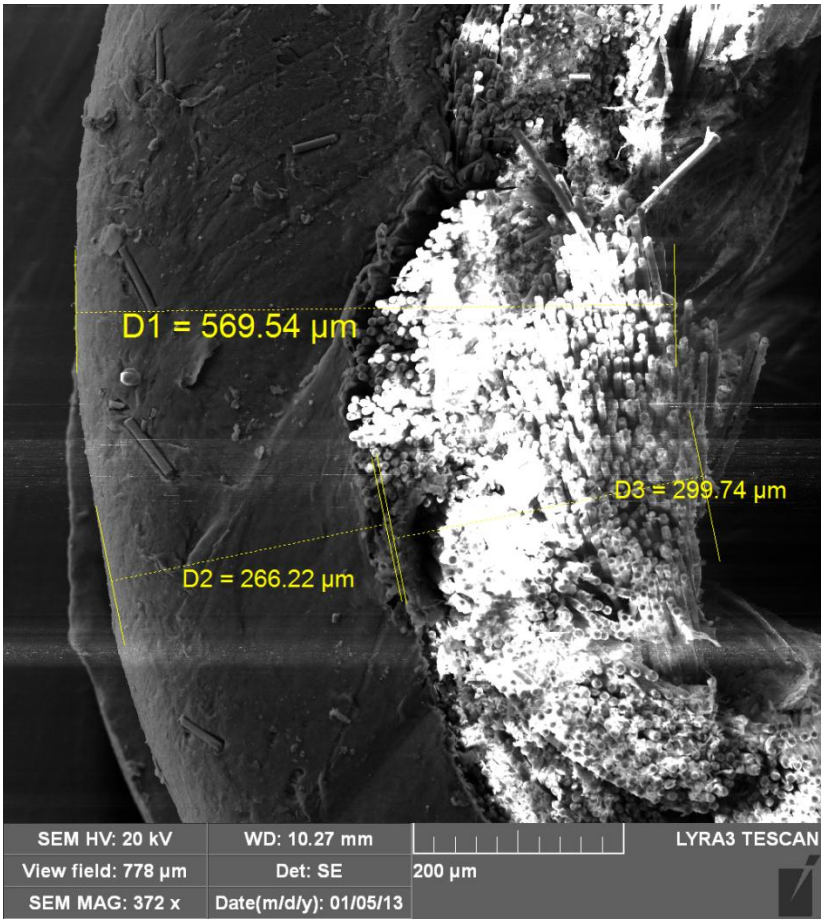


Figure 53: SEM image of HF porous membrane (thickness)

9.4 Kinetics study (order of reactions and permeability) of target sulfur compounds removal using porous membrane approach

Kinetics was studied to determine the types of the reaction order (1^{st} or 2^{nd}). The results indicated that most the target sulfur compounds removal using porous membrane assisted follow the 2^{nd} order reaction, as shown in Table 47-48. The order of the reaction was calculated using 1^{st} or 2^{nd} formula. The order of the reaction was calculated based on various concentrations versus times (second). Table 48 shows the results of target sulfur compounds permeability and diffusing coefficient using porous membrane assisted.

The permeability of sulfur compounds removal increases along with increasing the extraction time up to the optimum time (20 minutes) and then starts to decrease due to the performance of the membrane was reduced.

Table 47: Kinetics study (order of reaction) of target sulfur compounds removal using porous membrane assisted.

Sulfur compounds	300 s	600 s	1200 s	1800 s	3600 s	Order of reaction
2,6 DMBT	8.47E-11	1.4E-10	1.47E-10	8.13E-11	3.46E-11	Second order
2,4 DMBT	4.66E-10	3.85E-10	3.04E-10	1.41E-10	5.93E-11	do
2,3 DMBT	6.46E-10	4.57E-10	4E-10	1.68E-10	6.96E-11	do
2,3,6TMBT	6.39E-10	4.57E-10	2.66E-10	9.96E-11	4.22E-11	do
2,3,4 TMBT	6.83E-10	4.99E-10	3.45E-10	9.23E-11	3.49E-11	do
DBT	7.72E-10	6.16E-10	4.01E-10	2.54E-10	4.6E-11	do
4-MDBT	5.02E-10	3.78E-10	4.53E-10	2.15E-10	9.65E-11	do
1-MDBT	6.35E-10	4.47E-10	6.12E-10	2.53E-10	9.52E-11	do
4-ETH –DBT	2.97E-10	2.15E-10	4.7E-10	1.99E-10	6.21E-11	do
4-6 DMDBT	2.99E-10	2.36E-10	2.34E-10	1.31E-10	5.56E-11	do
2-4 DMDBT	3.25E-10	2.31E-10	2.44E-10	1.29E-10	5.57E-11	do
3-6 DMDBT	3.64E-10	2.78E-10	1.77E-10	9.86E-11	3E-11	do
2-8 DMDBT	2.2E-10	2.28E-10	1.69E-10	8.26E-11	3.45E-11	do
1-4 DMDBT	5.08E-10	4.14E-10	3.15E-10	1.76E-10	7.16E-11	do
1-3 DMDBT	7.53E-10	6.28E-10	3.36E-10	2.14E-10	1E-10	do
4-ETH -6-MDBT	6.76E-10	4.42E-10	2.81E-10	1.76E-10	8.42E-11	do
2 Prop DBT	2.06E-10	1.55E-10	1.14E-10	5.56E-11	2.38E-11	do
2-4-8 TMDBT	1.75E-10	1.4E-10	1.37E-10	6.66E-11	3.08E-11	do

Table 48: Kinetics study (permeability) of target sulfur compounds using porous membrane assisted.

Sulfur compounds	300 s	600 s	1200 s	1800 s	3600 s	Order of reaction
2,6 DMBT	5.08E-14	8.41E-14	8.84E-14	4.88E-14	2.07E-14	Second order
2,4 DMBT	2.8E-13	2.31E-13	1.82E-13	8.49E-14	3.56E-14	do
2,3 DMBT	3.88E-13	2.74E-13	2.4E-13	1.01E-13	4.17E-14	do
2,3,6TMBT	3.83E-13	2.74E-13	1.59E-13	5.97E-14	2.53E-14	do
2,3,4 TMBT	4.1E-13	3E-13	2.07E-13	5.54E-14	2.09E-14	do
DBT	4.63E-13	3.7E-13	2.41E-13	1.52E-13	2.76E-14	do
4-MDBT	3.01E-13	2.27E-13	2.72E-13	1.29E-13	5.79E-14	do
1-MDBT	3.81E-13	2.68E-13	3.67E-13	1.52E-13	5.71E-14	do
4-ETH –DBT	1.78E-13	1.29E-13	2.82E-13	1.19E-13	3.73E-14	do
4-6 DMDBT	1.79E-13	1.42E-13	1.41E-13	7.87E-14	3.34E-14	do
2-4 DMDBT	1.95E-13	1.39E-13	1.46E-13	7.73E-14	3.34E-14	do
3-6 DMDBT	2.18E-13	1.67E-13	1.06E-13	5.92E-14	1.8E-14	do
2-8 DMDBT	1.32E-13	1.37E-13	1.01E-13	4.96E-14	2.07E-14	do
1-4 DMDBT	3.05E-13	2.49E-13	1.89E-13	1.05E-13	4.3E-14	do
1-3 DMDBT	4.52E-13	3.77E-13	2.02E-13	1.28E-13	6.02E-14	do
4-ETH -6-MDBT	4.06E-13	2.65E-13	1.69E-13	1.06E-13	5.05E-14	do
2 Prop DBT	1.24E-13	9.27E-14	6.86E-14	3.34E-14	1.43E-14	do
2-4-8 TMDBT	1.05E-13	8.38E-14	8.24E-14	3.99E-14	1.85E-14	do

CHAPTER 10

10.0 Conclusion and Recommendations

10.1 Conclusion

The sulfur, nitrogen and mercury compounds in petroleum products are main source for harmful emissions. These emissions are extremely harmful to environment and contribute into environment pollutions. Currently, the sulfur and nitrogen containing compounds are treated at industrial level using conventional method by catalyst named cobalt-molybdenum at high temperature, pressure and hydrogen consumption, but this techniques has no ability to extract various sulfur and nitrogen compounds such as dibenzothiophen and its derivates and carbazol and its derivatives. Accordingly, various alternative techniques named non-conventional methods have been investigated for sulfur and nitrogen compounds removal such as adsorbent, direct liquid- liquid extraction, biodesulfurization and novel catalyst. For the first time, a novel micro-extraction was developed using LPME-HFM for sulfur containing compounds determination. The method was investigated and applied on heavy, medium and light crude oils as well as fractions. The results showed that this LPME-HFM method is promising for sulfur compounds determination with high recovery > 80 % and has coefficient of determination (R^2) in the range of 0.9967 to 0.999. The linearity response of this method was excellent for all target sulfur analytes in a range between 1 and 500 ppm with high reproducibility. The detection limits were 100 ppb. The results obtained using this method was comparable with ASTM method.

In addition, dispersive liquid-liquid micro-extraction (DLLME) has been examined for sulfur containing compounds removal from diesel. In this method various organic solvents and ionic liquids such as furfural, methyl furfural and n-methyl pyrrolidone and [EMIM][CF_3SO_3] were investigated . This method has also shown high recovery for sulfur compounds in petroleum products using combined methyl pyrrolidon with ionic liquid [EMIM][CF3SO3] with ultrasonication. This method was linear with high correlation factor ranges from 0.9967-0.9998. The detection limits were 1-100 mg/L. However, it was noticed that this method can be used only for clean samples and not suitable for crude oil samples.

Moreover, simultaneous removal of sulfur and nitrogen and mercury containing compounds using electromembrane assisted flow reactor was evaluated. The conditions of this method was optimized using the proper ratio between ionic liquid with organic solvent 1:10 [EMIM][CF3SO3]: (n-methyl pyrrolidone), flow rate 10 rpm, extraction optimum time 20 minutes, sample volume, extractive solvent volume and applied voltage 100 v. The results revealed that the removal percentage of target sulfur compounds from real diesel, heavy, medium and light crude oils were 44, 48, 53 and 57%, respectively. Also, the results showed that removal of nitrogen and mercury compounds form crude oils and fractions were also achieved using this novel method. The results indicated that the percentage of total nitrogen removal from light, heavy crude oils and diesel was 49, 44 and 33 %, respectively. Moreover, the mercury was reduced from 0.5 ppm to 0.27 and 1 ppm to 0.57 ppm (~ 50%). X-ray fluorescence and FT-ICR-MS were used to confirm the sulfur compounds extraction results obtained by using gas chromatography equipped with sulfur detector.

10.2 Recommendations

The desulfurization and denitrogenation process using electromembrane flow reactor should be up-scaled from the laboratory scale to a pilot plant with a solvent extraction and regeneration process column. This process should also be followed by selective adsorbent to enhance the sulfur, nitrogen and mercury compounds recovery. Various porosity and thickness of membrane should be evaluated for sulfur, nitrogen and mercury compounds removal from crude oils and petroleum products (kerosene, gasoline and naphtha). Synthesized organic solvents and ionic liquids which have more solubility for sulfur compounds should be taken in consideration. In addition, the novel process should be examined at elevated temperatures (50 and 100 º C) to increase the efficiency for sulfur, nitrogen and mercury compounds removal and evaluate the process impact on aromatic, oxygenated compounds, metals and aliphatic compounds removal.

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2- Determination of sulfur compounds in crude oils and fractions using liquid-phase micro-extraction approach.

3- Monitoring CO_2 absorption and desorption by FTIR-ATR and NMR using various organic solvents.

4- Simultaneous removal of sulfur and mercury using electro-porous membrane assisted flow reactor.

5- Determination of sulfur compounds in crude oils fractions using dispersive liquid-liquid micro-extraction method.

6- Thermal characterization of solid material using TGA-MSD